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OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

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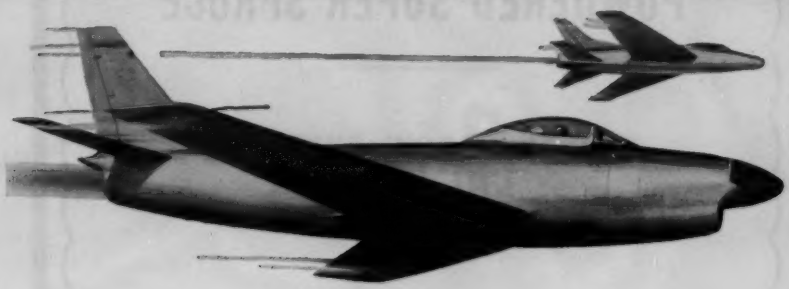

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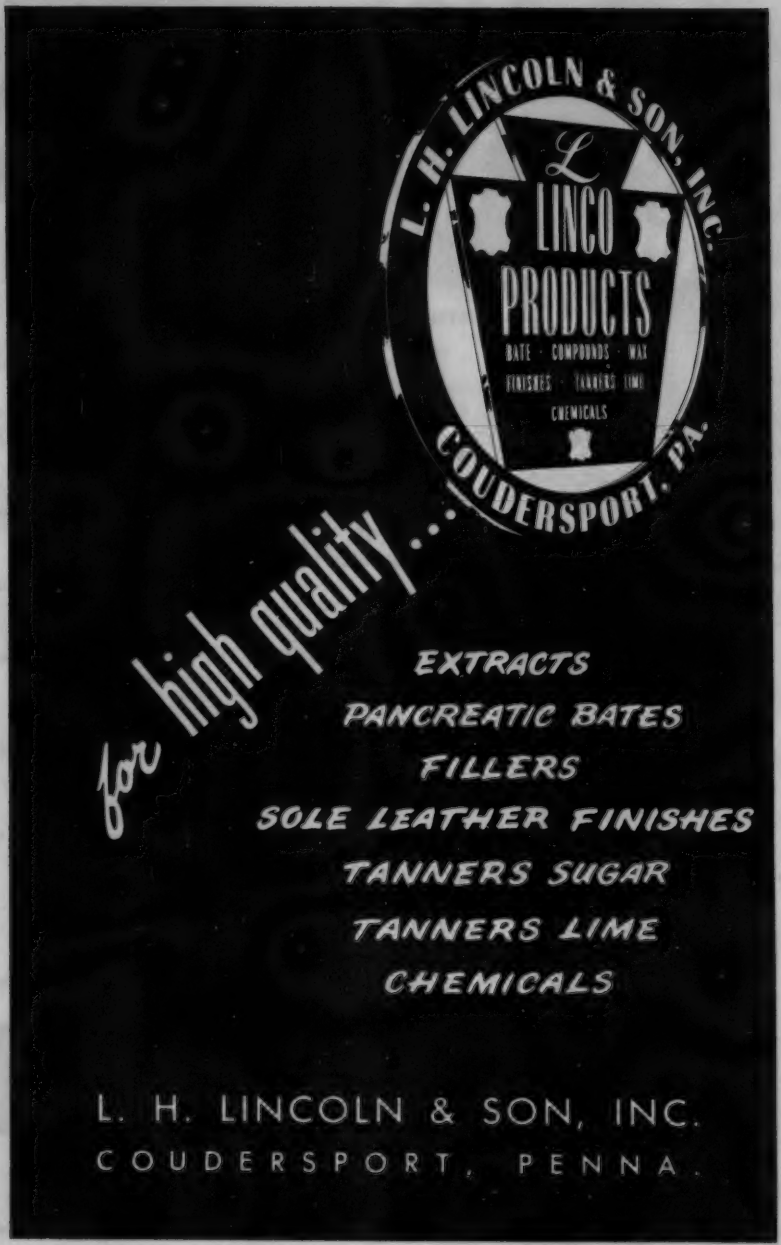
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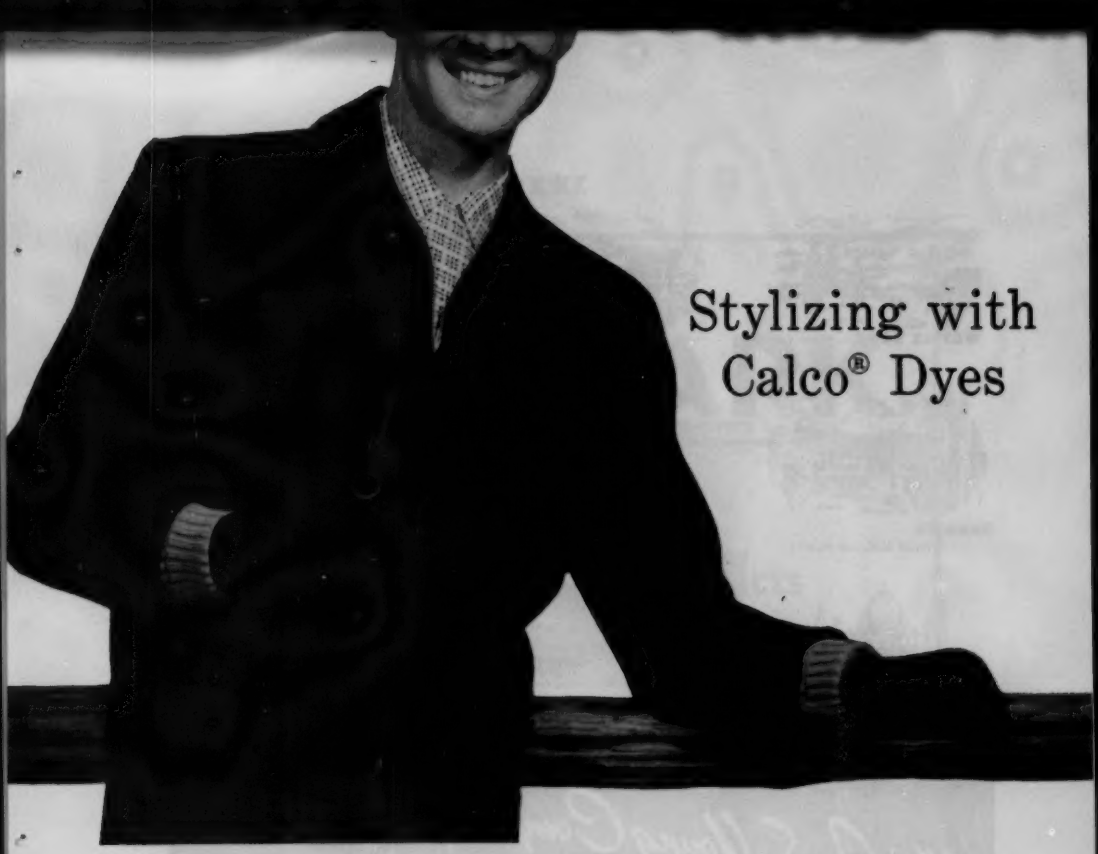

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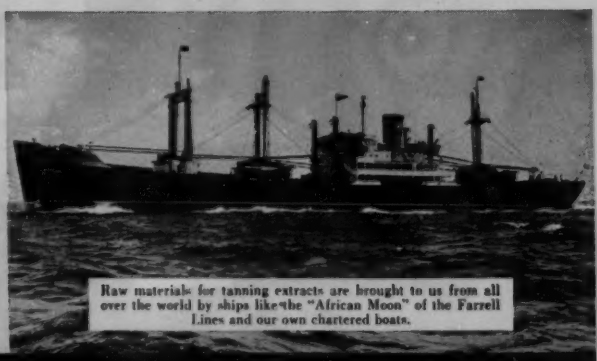

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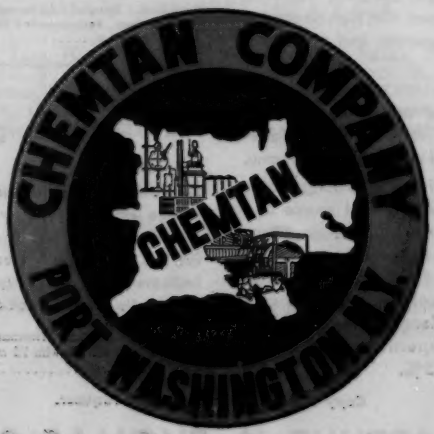

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Vol. L JUNE 1955 No. 6

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Unhairing of Hides and Skins by Amylase Preparations

By THEONE C. CORDON

*Eastern Regional Research Laboratory**
Philadelphia 18, Pennsylvania

The use of enzymes for unhairing hides and skins dates back to antiquity, for the bacteria that are active in the old-time sweating process accomplish their action by means of the enzymes which they elaborate. Isolated enzymes were first used successfully by Otto Röhm in 1910[4] when he found that the use of pancreatic enzymes for bating could be extended to unhairing if the skins were first swollen in an alakli solution such as soda, ammonia, or borax and neutralized with sodium bicarbonate.

Since this original work of Röhm's numerous attempts have been made to utilize plant, animal, and microbial enzymes for unhairing hides and skins. Green[3] has recently reviewed the literature including the patent literature, and, according to him, a mold enzyme process is now in use in Germany for the manufacture of glacé kid. This is the only instance of the commercial use of isolated enzymes that has been noted. Most tanners believe that enzymes do not give uniform hair loosening or are difficult to control or are too costly.

In 1953 Burton, Reed and Flint[1] suggested a novel approach to the unhairing problem. They stated that all fibrous protein structures are in close association with mucoids; thus such material is present in the spaces between the corium fibers and especially at the epidermal-corium junction and around the hair follicles. They suggested that mucoid material may play an important part in the lime yard processes and that soaking back, unhairing and bating may, in essence, be the removal of this material. On the basis of this thesis they tried what they termed mucolytic enzymes such as pectinase, diastase and pancreatic elastase and found that these enzymes removed the hair

*A laboratory of the Eastern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

from fresh calfskin at room temperature in about 3 days. Testicular hyaluronidase was incapable of unhairing fresh calfskin over the pH range of 5.2 to 7.5. No details are given as to how the experiments were conducted.

Not long after the paper by Burton, Reed and Flint (loc. cit.) appeared, Gillespie [2] published a paper in which he described the depilation of sheepskins by enzymes from certain fungi. Commercial preparations of papain, trypsin, pancreatin, chymotrypsin, pepsin, erepsin, amylase, lipase, malt diastase, takadiastase, arazyme N and oropon F were also tried. None of these commercial preparations showed any activity in the presence or absence of activators. The enzymes were applied to the flesh side of the sheepskins in the form of a clay paste. It is doubtful if Burton et al. (loc. cit.) used this procedure, so their results may not be comparable. Gillespie suggested that the unhairing action found by Burton et al. (loc. cit.) was due to the action of contaminating bacteria. He stated that pectinases and diastases would not be expected to attack the mucoid materials as postulated by Burton et al. (loc. cit.) nor would mucolytic enzymes be expected to be present in such preparations.

Experimental

Preliminary trials were made with commercial amylase preparations on salted hide. The preparations tried are listed in Table I. This salted hide was used because it was immediately available although it had been in storage for some time at 35 – 40° F. and was showing hair slip in spots. Only pieces that had tight hair were used for testing. Although there were differences in the effectiveness of various samples of enzymes, all caused some hair loosening and some were very effective, causing the hair to become extemely loose in 16 hours. It was evident very early that bacterial growth must be prevented because bacteria could cause hair loosening and thus invalidate the results.

TABLE I

Amylase Preparations Tried as Unhairing Agents

Enzyme Preparation	Source	Origin, where known
Special Diastase 160	Takamine Laboratories	——
RT-44	" "	Bacterial
Clarase 300	" "	Fungal
Pancreatin 3 USP	" "	Animal
Rhozyme 51	Rohm and Haas Company	——
Rhozyme DX	" " " "	——
Rhozyme S	" " " "	——
Mylase SA	Wallerstein Laboratories	Fungal (Aspergillus oryzae)
Enzyme W3F	" "	——
Enzyme 164	" "	——
Mylase L-1	" "	——

Several antiseptics were tried including the usual toluene. The most effective was phenyl mercuric acetate in a concentration of 0.15 gram per liter. Although sodium chloride precipitates this material, it still maintains sterility for at least 3 or 4 days. This antiseptic was used in all tests.

Since Burton, Reed and Flint (loc. cit.) had used fresh hide, it was deemed advisable to try the process on fresh, unsalted hide. A medium weight cowhide was obtained from a slaughterhouse shortly after it was flayed. It was washed in a drum for 1 hour, fleshed, cut in strips and quick frozen in a deep freeze chest. Strips were removed and thawed as needed.

When this fresh hide (before or after freezing) was treated with the commercial amylase preparations there was little or no hair loosening. It was soon discovered that pretreatment of fresh hide with sodium chloride solution would render it susceptible to action of some diastase preparations and that 2 to 3 per cent salt was more effective than 5, 10 or 20 per cent.

The following experiment illustrates the effect of pretreatment with salt. Four 1½″ x 3″ pieces of fresh, frozen cowhide were thawed and weighed. Each piece weighed 30 grams. One piece was placed in 200 ml. of each of the solutions shown in Table II. All the solutions contained 0.15 gram per liter of phenyl mercuric acetate. The solutions and hide pieces were in rectangular pint jars, which were placed in a constant temperature oven equipped with a device for rotating the jars at 9 - 10 RPM on their long axis. The temperature was kept at 38° C. After 24 hours' incubation the solutions were drained from the jars of treatment numbers 1 and 2 (Table II) and a 0.25 per cent

TABLE II

Effect of Sodium Chloride on the Unhairing Action of "Special Diastase"

		Degree of Hair Loosening* at Hours Incubation		
No.	Treatment	24	48	72
1	Antiseptic 24 hours followed by 0.25% diastase	0	+	++
2	2% NaCl 24 hrs. followed by 0.25% diastase	0	+++	+++++
3	0.25% diastase	0	0	+
4	2% NaCl + 0.25% diastase	0	++	+++

*Rated 0 to +++++, where +++++ = hair completely loose.

diastase preparation* was added. There was little hair loosening except where salt was used. Pretreatment with salt was more effective than adding it with the enzyme. This may be due to the fact that a certain time is required for the salt to act before the enzyme can act. During this time the enzyme may be losing activity. In some experiments a slight hair loosening was produced simply by washing the hide in the antiseptic solution for several days.

*The preparation used was "Special Diastase 160" sold by the Takamine Laboratories.** It is described as a "Unique formulation of various diastases" . . . containing "buffering, activating and stabilizing salts".

**In mentioning trade names the Eastern Utilization Research Branch, United State Department of Agriculture does not in any way guarantee the products nor are they recommended in preference to others not mentioned.

The possibility of a depilatory enzyme being present in the skin is thus suggested. This point is under investigation.

Numerous attempts have been made to produce this enzyme unhairing without sodium chloride. Activators such as cysteine, sodium sulfite, and sodium sulfide, which were used by Gillespie (loc. cit.) were tried but had no effect. Pretreatment with dilute (1-2%) urea was almost as effective as sodium chloride.

On the theory that the enzyme must penetrate to the site of action from the flesh side (as it must in Gillespie's test), successive layers of corium were split off. There was no apparent effect upon the hair loosening by the enzyme whether most of the corium had been removed or not.

The effect of agitation and flexing is shown in Table III. Fresh, frozen calfskin was thawed and placed in a 2 per cent sodium chloride solution containing 0.15 gram per liter of phenyl mercuric acetate and allowed to stand for 2 days. Another piece of fresh, frozen calfskin was taken from the freezer to serve as the unsalted control. One piece of salt-treated and one of fresh skin were incubated under the conditions shown in Table III in solutions of a 0.25 per cent diastase preparation.* The effects of salt treatment and flexing are shown very well by these results.

TABLE III

The Effect of Agitation and Flexing on the Unhairing Action of "Special Diastase"* on Calfskin

No.	Treatment	Degree of Hair Loosening at Hours Incubation		
		24 Temp. 24° C.	48 Temp. 24° C.	72 Temp.**
1	Stationary			
	Salt treated	0	0	+
	Not salt treated	0	0	0
2	Agitated in "Rotor oven"			
	Salt treated	0	0	+++++
	Not salt treated	0	0	++
3	Flexed at 88 strokes per min.			
	Salt treated	+	+	+++++
	Not salt treated	0	0	0

*0.25% solution.

**Since the action was so slow at 24° C., the temperature was increased to 30° in the agitated samples and to 27° in the others.

Summary

At present it appears that enzymes are unable to penetrate to the hair roots without the previous action of sodium chloride, urea or perhaps other materials. The function of these substances, is, as yet, not clear, but it appears that they dissolve some constituent of the hide which prevents the action

of the enzyme. Also, it is not known as yet what enzymes are responsible. Commercial amylases are certainly not single enzymes, and it may well be that on entirely unsuspected enzyme is responsible for the depilatory action. It is hoped that light can be thrown on this question by future work. It has been found that some reducing substance, presumably sugar, is produced by the action of enzymes on hides. So far we have not been able to demonstrate any correlation between this "sugar" release and the looseness of the hair.

Acknowledgment

The author wishes to thank the Rohm and Haas Company, the Wallerstein Company, and the Takamine Laboratories for supplying samples of their amayse preparations.

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Coefficient of Friction (Static) for Glove Materials On An Automobile Steering Wheel

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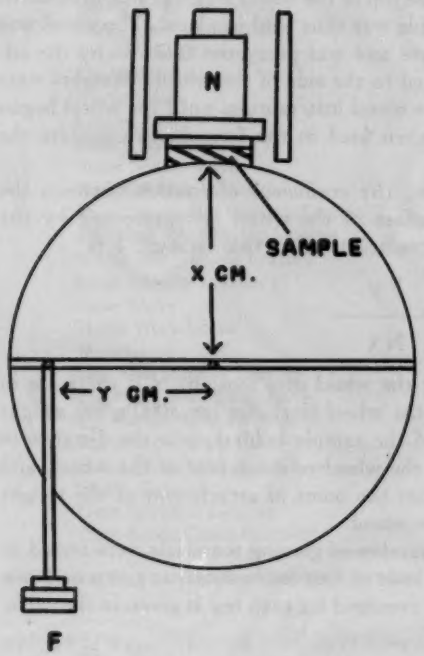
The gripping ability of the hands on the steering wheel of an automobile is an important factor concerning with safety in driving. Since many people wear gloves for driving, particularly when the weather is cold, the gripping ability of leather gloves in comparison to gloves made of other materials is an important concern to the public and safety organizations. It is of interest to the leather industry in its constant research program to improve its products. For studying this property, a method for measuring the coefficient of friction between the surface of a gloving material and the surface of an actual steering wheel was developed.

Experimental

There are many methods of measuring the coefficient of friction but it seemed best to design an apparatus where a steering wheel would be used. The apparatus as designed is shown in the diagrammatic drawing in Figure 1.



N—Force Holding Sample Against Wheel (Constant)

F—Force Needed to Move Wheel (Variable)

x—Distance from Perimeter to Center of Wheel

y—Distance from Point of Attachment of the Weight Suspension Arm to the Center of the Wheel.

FIGURE 1.—Diagram of Apparatus Used for Measuring the Coefficient of Friction Between the Surface of a Gloving Material and the Surface of a Steeering Wheel.

It consisted of a modern plastic automobile steering wheel which was mounted on a shaft perpendicular to the wheel. The shaft fit horizontally into a long metal pipe which was slightly larger in its inside diameter than the shaft so that the wheel had a solid support but was free to rotate in either direction. Grease was used to lubricate the shaft in the pipe to eliminate friction due to the rotation of the shaft itself. To the stand, which supported the wheel, a frame was fastened so that the sample to be tested, sample holder, and a 5000 gram weight could be held stationary on top of the steering wheel. The sample holder was a block of wood which was grooved similarly to the contour of the palm of the hand when gripping the wheel. To further simulate the hand a

thin piece of foam rubber was used to line the grooved area so the samples would not be fastened directly against the hard wood sample holder. With this apparatus, gloves or pieces of leather and other fabrics were evaluated for their coefficients of friction.

In running the test, the sample was tacked to the grooved block, the block was placed in the holder space at the top of the wheel and was weighted down by the 5000 gram weight; the sample was thus held in place. The wheel was the object that was allowed to move and was prompted to do so by the addition of weights to an arm attached to the side of the wheel. Weights were added carefully, so as not to jar the wheel into motion, until the wheel began to move. This total weight was then used in the formula to calculate the coefficient of friction.

The formula used for calculating the coefficient of friction between the surface of the sample and the surface of the wheel is represented by the following formula, where μ is the coefficient of friction (static); F is

$$\mu = \frac{F\,y}{N\,x}$$

the force in grams needed to start the wheel into motion; N is the force in grams holding the sample against the wheel (includes the 5000 gram weight and the weights of the sample and the sample holder); x is the distance in centimeters from the perimeter of the wheel to the center of the wheel; and y is the distance in centimeters from the point of attachment of the weight suspension arm to the center of the wheel.

The coefficients of friction of a number of gloving materials were tested as well as the gripping power of the hands of four individuals, as given in Table I. Four to six tests were made and averaged for each result given in the table.

Discussion of Results

The results for the coefficients of friction are given in Table I and show a considerable difference between the samples tested. The value for the surface of a bare hand was 1.33 in the case of a less resistive hand and 1.57 in the case of a more resistive hand. The hand was tested similarly to the samples, being held stationary on the top of the wheel, with the 5000 gram weight as the force "N". The value nearest the value for the hand with no glove would seem to be the most ideal; therefore a value of 1.+ would indicate a satisfactory friction and values less than 1. would be less satisfactory with values less than 0.5 constituting a hazard in the safety of driving.

The values for wool and the fabrics—rayon, cotton and nylon—were quite low ranging from 0.30 to 0.44 in their coefficients of friction. This indicates that they have little gripping power in contrast to the bare hands

TABLE I

Coefficients of Friction (Static) for Glove Materials on an Automobile Steering Wheel

Bare Hand—Subject I	1.57
Bare Hand—Subject II	1.57
Bare Hand—Subject III	1.33
Bare Hand—Subject IV	1.33
Beige Wool Glove	0.39, 0.41
Green Wool Glove	0.37, 0.30
Rayon Glove	0.41, 0.46
Cotton Glove	0.44, 0.36
Heavy Nylon Glove	0.44, 0.38
Sheer Nylon Glove	0.35, 0.31
Red Kid Gloving Leather	1.30, 1.34
Inca Copper Kid Gloving Leather	1.41, 1.16, 1.30
Dip Blue Kid Gloving Leather	1.27, 1.20
White Kid Gloving Leather	1.18, 1.16
Cape Gloving Leather	1.24, 1.27
Cape Glove	1.59, 1.37
Horse Work Glove	1.31, 1.21
Deer Glove	1.11, 1.11
Doe Skin Gloving Leather	0.97, 1.01
Pig Skin Gloving Leather	1.14, 1.14
Pig Glove—Unworn Area	0.88
Pig Glove—Worn Palm	0.90
Sheep (Simulated Pig) Glove	1.12, 1.25, 1.29
Sheep Glove	1.09, 1.07
Goat Garment Leather	1.13
Cape Suede Glove Leather	0.88, 0.92

Note—Four to six tests were made and averaged for each result expressed above.

which has a coefficient of friction of over 1. The leather samples tested gave values which were much higher than wool and the fabrics tested, particularly horse work gloves and kid and cape skin leathers. The values for these leathers ranged from 1.16 to 1.59. Deer, doe, pig, sheep, goat and cape suede leather gave slightly lower values than the horse work glove and the kid and cape skin leathers but were still superior to the fabrics and wool; the range in values was from 0.88 to 1.29.

Summary

1. The bare hand on the steering wheel has good gripping power.

2. Horse work gloves and kid and cape skin leather gloves are good gloves for driving since they have gripping abilities comparable to the bare hand on the steering wheel, under the conditions of testing,

3. Deer, doe, pig, sheep, goat, and cape suede leather gloves have good gripping abilities but were not as good as the horse work gloves and the kid and cape leather gloves tested.

4. Wool and the fabrics—cotton, nylon and rayon—had poor gripping abilities under the conditions of testing.

Conclusion

In conclusion this work indicated that leather gloves have more gripping ability and thus should be safer for driving than gloves made of wool and other fabrics.

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Protein Constituents of Calfskin Through Beamhouse Processes

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Introduction

The proteins of skin or hide as they are influenced by beamhouse processes have been traced by histological and chemical methods to give an insight into their general distribution and approximate prevalence. Other than the work of Rosenthal [1] and McLaughlin and Theis [2] who made attempts at analyzing skin or hide, investigators such as Kritzinger [3], Roddy and Hermoso [4], and Roddy and Pandit [5] have based their chemical examination on the proteins expressed in the beamhouse liquors rather than those proteins remaining in the stock after each operation.

Roddy [6], [7], however, did study the coagulable proteins and elastic tissue of skin through process by histological techniques. His findings gave a qualitative understanding as to the location of these proteins and an indication as to their change due to process.

The presence of globular proteins, elastic tissue and other proteins left in the skin after the beamhouse processes is important in contributing to the character of the final leather. It was shown by Roddy and Hermoso [4] that a good removal of coagulable proteins from skin or hide results in leather that has a better yield; Roddy [7] found that elastic tissue becomes unyielding and brittle after chrome tanning.

Since all of these proteins are important, protein fractionation methods were used to determine the quantitative changes occurring in these constituents of calfskin from fresh stock through curing, soaking, liming, bating and pickling and to show the degree of purification of the leather making substance—collagen. The method used for determining the protein constituents was that developed by the author[8] and four fractions were obtained. Hair, epidermis, elastic tissue and unextractable globular proteins are reported in fraction I; extractable globular proteins composed of entities referred to as albumins, globulins and mucoids (coagulable proteins) in fraction II; collagen in fraction III; and non protein nitrogen such as urea or amino acids in fraction IV.

Experimental

A fresh calf skin was obtained immediately after the animal was flayed. Samples of the fresh skin were taken; the skin was then brine cured in a saturated salt solution for two days and then stored for one month in a refrigerator at 40° F., no additional salt being put on the skin before storage.

At the end of one month in storage, the brine cured skin was still soaked for 18 hours in distilled water at 70° F., with a float ratio of 4 to 1; the soak water was changed at the end of the twelfth hour of soaking. The soaked skin was still limed for three days in sodium sulfide (0.25 per cent on soaked skin weight) and calcium hydroxide (4 per cent on soaked skin weight), with a float ratio of 4 to 1. The limed skin was unhaired, fleshed and then bated in Oropon C (0.25 per cent on limed skin weight) for 1½ hours at 100° F., with a float ratio of 8 to 1. The skin was pickled in 12.5 per cent sodium chloride on the solution basis and 1.5 per cent sulfuric acid on the skin basis, with a float ratio of 2 to 1. The bating and pickling operations were carried out in a "Launderometer"; at the end of the two hour pickling period, the agitation was stopped and the skin stood overnight in the pickling liquor.

Samples for analysis were taken from seven positions of the skin after each operation—control, brine cured-stored one month, soaking, liming, bating and pickling. Seven samples, 2 by 2.5 inches, one from each of the seven positions, were removed at the finish of each operation; the rest of the skin was further processed. Figure I shows the seven sampling positions, four positions being along the upper portion of the skin from neck to tail, three being along the lower portion of the skin from the front leg to the back leg, respectively. Figure I also shows the detail of the specimens in each position. A control sample was taken close to the center of each sampling position, "A" in Figure I, so that each of the following samples taken could be compared directly to the control to avoid areawise variation as much as possible. The samples were taken after cure of one month, soaking, liming, bating, and pickling in positions "B", "C", "D", "E" and "F", respectively. These samples were held, until analysed, in moisture tight containers in a deep

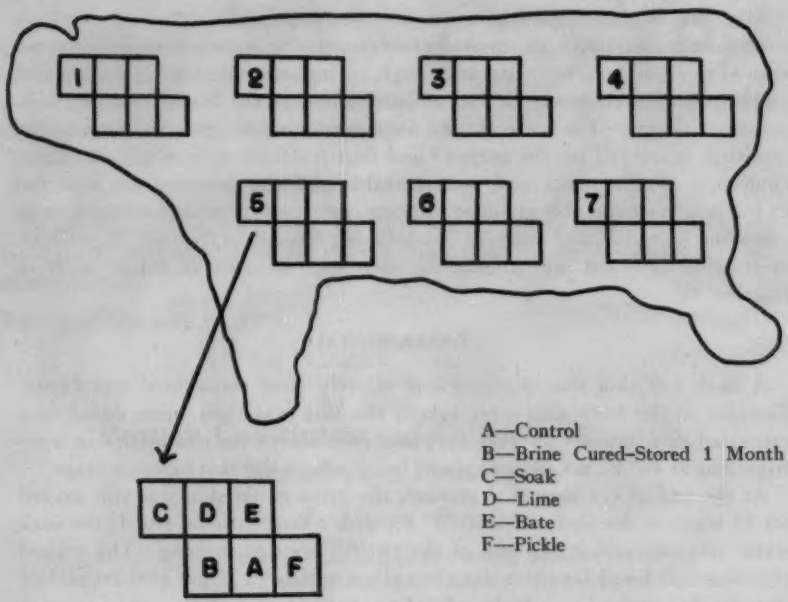

FIGURE 1—Diagram of Sampling of the Calfskin Showing the Seven Sampling Positions and the Detail of Each 2x2½ Inch Specimen.

freeze cabinet at 0°F. Before being analysed, samples "A", "B", and "C" were clipped of hair and all samples were fleshed. A complete protein fractionation was then made in duplicate, each sample being analysed for elastin, keratin, epidermis and unextractable globular protein nitrogen, extractable globular protein nitrogen, collagen nitrogen, and non protein nitrogen.

Results

The results of the fractionation are given in Table I and are reasonable in relationship to areawise variation and distribution of the tissues as indicated by histological examination of calfskin. The *fresh* stock showed considerable areawise variation of the globular protein nitrogen. Going across the upper portion of the skin from the neck area to the butt, the amount of nitrogen derived from globular proteins decreased accordingly 15.3, 14.2, 13.5 and 12.4 per cent. The same was true in the lower portion of the skin where the decrease was 13.9, 12.5 and 11.5 per cent, respectively going from the fore flank to the rear flank of the skin.

TABLE I

Fractionation of the Calfskin through Beamhouse Processes

	Position	Fresh	Cured	Soaked	Limed	Bated	Pickled
Fraction I							
Elastin	1	8.9%	13.0%	8.9%	1.2%	2.8%	2.5%
Keratin	2	11.4	15.2	15.8	3.0	3.4	2.3
Epidermis	3	10.6	15.5	14.1	2.5	2.8	2.2
Unextractable	4	12.8	17.5	12.8	2.2	3.7	2.7
Globular	5	11.2	——	17.1	2.1	2.2	2.4
Protein	6	12.0	——	13.8	1.9	2.1	2.1
Nitrogen	7	12.4	——	13.9	2.8	2.6	2.3
	Av.	11.4	——	13.8	2.2	2.8	2.4
Fraction II							
Extractable	1	15.3	6.6	7.6	3.9	1.7	0.2
Globular	2	14.2	8.8	10.8	4.1	2.1	1.9
Protein	3	13.5	7.6	10.7	5.4	2.4	1.0
Nitrogen	4	12.4	5.3	9.6	3.8	2.3	2.5
	5	13.9	——	9.3	3.4	1.5	1.9
	6	12.5	——	8.5	4.4	1.8	1.2
	7	11.5	——	9.5	4.0	1.6	1.8
	Av.	13.3	——	9.4	4.2	1.9	1.5
Fraction III							
Collagen	1	73.4	78.6	82.3	93.1	93.9	96.7
Nitrogen	2	71.8	73.5	71.2	90.6	92.9	95.0
	3	74.1	74.7	73.5	90.2	93.2	96.1
	4	72.6	75.2	76.2	92.5	92.8	92.4
	5	——	——	71.7	93.0	94.8	92.7
	6	73.2	——	75.8	92.2	94.7	94.5
	7	73.8	——	74.6	91.8	94.6	93.0
	Av.	73.1	——	75.0	91.9	93.9	94.3
Fraction IV							
Non	1	2.4	1.8	1.2	1.8	1.6	0.6
Protein	2	2.6	2.5	2.2	2.3	1.6	0.8
Nitrogen	3	1.8	2.2	1.7	1.9	1.6	0.7
	4	2.1	2.0	1.4	1.5	1.2	2.4
	5	—	—	1.9	1.5	1.5	3.0
	6	2.3	—	1.9	1.5	1.4	2.2
	7	2.3	—	2.0	1.4	1.2	2.9
	Av.	2.2	—	1.8	1.7	1.4	1.8

Note.—Each result expressed above is the average of duplicate tests and represents the percentage of the total nitrogen of a skin sample that is in a fraction.

There was also considerably areawise variation in the residue nitrogen. Going along the upper portion of the skin from the neck area to the butt, the amount of nitrogen derived from elastin, keratin, epidermis and unextractable globular proteins increased, 8.9, 11.4, 10.6 and 12.8 per cent. Along the lower portion of the skin from the fore flank to the rear flank, the increase was 11.2, 12.0 and 12.4, respectively.

There was little areawise variation of collagen and non protein nitrogen. The amount of collagen nitrogen was 73.4, 71.8, 74.1, 72.6, 73.2, and 73.8 per cent of the total nitrogen in the areas tested; non protein nitrogen was 2.4, 2.6, 1.8, 2.1, 2.3 and 2.3 per cent in the areas tested.

The noticeable effect of *curing* compared to fresh skin was the denaturation of the globular proteins. They were not extracted from skin residue material, particularly the epidermis. Fractions I and II both were affected; fraction I containing the elastin, keratin, epidermis and unextractable globular protein nitrogen increased from 8.9, 11.4, 10.6, and 12.8 per cent to 13.0, 15.2, 15.5, and 17.5 per cent, respectively, in the areas tested; fraction II containing the extractable globular protein nitrogen decreased from 15.3, 14.2, 13.5, and 12.4 per cent to 6.6, 8.8, 7.6, and 5.3 per cent, respectively. However, if these two fractions are added together, it is seen that the sums for the brine cured samples have changed very little over the sums for the fresh samples except for a small decrease in positions 2, 3, and 4 and considerable decrease in the neck position (position 1) which decrease apparently was due to a loss of globular proteins. The sums for these four areas in the fresh skin are 24.2, 25.6, 24.1, and 25.2 per cent and in the brine cured skin are 19.6, 24.0, 23.1, and 22.8, respectively. It is apparent that denaturation occurred and the globular proteins were not completely removed from the epidermis, the germinating cells, stratum germinatum, in particular.

It is a known fact that brining can remove some globular proteins and this was true for the skin studied. As mentioned above there was an apparent loss of globular proteins. The collagen nitrogen increased slightly after the curing compared to the collagen nitrogen in fresh skin which further indicates a loss of globular proteins. Non protein nitrogen changed very little.

From these results on brine cured calfskin it can be seen that since the collagen nitrogen fractions were 78.6, 73.5, 74.7, and 75.2 per cent of the total nitrogen that the tanner buys an impure product in respect to collagen. Only about three-fourths of the nitrogen he buys is leather making substance and considerable purification of this substance is done in the beamhouse.

The results of the *soaking* operation showed some solubilization of the denatured globular proteins since the extractable globular protein nitrogen values again increased. The globular protein nitrogen results while low are not too low considering the fact that the brining and soaking operations remove globular proteins. Since non protein nitrogen decreased slightly as

well as the globular protein nitrogen after soaking in comparison to the nitrogen values of fresh skin, the residue nitrogen and collagen nitrogen naturally have increased. The results show that the leather making collagen has been purified slightly by the soaking operation.

Liming, unhairing and *fleshing* of the skin produced a very noticeable change in the skin proteins. Fraction I decreased from 11.4 per cent in the fresh skin to 2.2 per cent in the limed skin, a decrease of 9.2 per cent. This decrease obviously represents hair and epidermis. The 2.2 per cent nitrogen remaining as residue was observed microscopically to be mainly elastic tissue with a very slight residue of debris left jn the hair follicles.

The extractable globular protein fraction was also reduced considerably, decreasing from 13.3 per cent in fresh skin to 4.2 per cent in limed skin, a decrease of 9.1 per cent. This decrease was partly due to the removal of the epidermis which contained denatured globular proteins in the cells and partly to the removal of globular proteins from the skin itself. But even after liming there were still globular proteins in the skin, representing 4.2 per cent of the total nitrogen.

The proportion of collagen nitrogen increased to 91.9 per cent after liming as compared to 73.1 per cent in the fresh skin. A considerable purification of the collagen has been accomplished as a result of the liming, unhairing and fleshing operation. Non protein nitrogen did not change as a result of liming.

Bating with a quarter of a per cent Oropon C resulted in further purification of the collagen. A significant amount of the globular proteins was removed, decreasing from 4.2 per cent in the limed skin to 1.9 per cent after bating. The residue of elastin and hair pocket debris was still present after bating and non protein nitrogen did not change. Because of the removal of globular proteins, the collagen nitrogen increased from 91.9 to 93.9 per cent of the total nitrogen.

Pickling produced still more purification of the collagen; the collagen nitrogen increased from 93.9 to 94.3 per cent. The elastin and hair pocket debris nitrogen and non protein nitrogen changed very little. The extractable globular protein nitrogen decreased from 1.9 per cent after bating to 1.5 per cent after pickling. However, it is noted that after pickling the skin was still not pure collagen but contained residual elastic tissue, hair pocket debris, globular proteins and non protein nitrogen to the extent of 5.7 per cent of the total nitrogen. This undoubtedly has an influence on the character of the leather which could be produced. It is not certain that it is desirable to entirely purify the collagen.

Discussion

Since use of the procedure has resulted in further knowledge, a classification and discussion of the proteins involved seems appropriate at this time.

Although this classification may disagree with work by previous investigators, it must be remembered that the method used is not the conventional method of the biochemists, that is, salt extraction, acid precipitations, etc. The method involves no salt, except that normally in the skin, and the absence of this salt may make the globular proteins behave differently than their conventional behavior in the acid solution.

Fraction I is the residue obtained after the sample is digested for one hour in 0.1 per cent hydrochloric acid at 85°C. This residue contains elastic tissue, epidermis, hair and unextractable globular proteins.

Elastic tissue is that fibrous material which natively is light yellow in color and stains with Weigert's elastic tissue stain. It is located predominently in the epidermal area of the skin, with only a small amount in the corium area. It is also located in the arteries of the blood vessel system. This material, including the arteries, was identified microscopically in the residue.

This elastic tissue was seen in the residue after each process—fresh, cure, soak, lime, bate and pickle. This is in accordance with the work of Roddy and O'Flaherty [7] who used Weigert's elastic tissue stain to study elastic tissue and showed that in fresh calfskin it is located in the epidermal area as a fine fibrous network surrounding the hair pockets, in all arteries larger than capillaries, scattered throughout the corium as isolated fibers and intermingled with the subcutaneous adipose tissue (flesh). Through process these fibers can be stretched or swelled, and broken from their points of attachment but are not removed from the skin. Hollander [9] also reported the presence of elastic tissue in skin after bating with proteolytic enzymes.

Epidermis is the covering of the skin and consists of four cellular layers, the corneum, lucidum, granulosum and germinativum. It also invaginates into the skin forming the hair pocket lining. This material was identified microscopically in the residue. The globular proteins of the epidermis, however, particularly those of the germinating layer were extracted, by the procedure, in part at least. Evidence of this is supported by the fact that fresh epidermis, that was not defatted with alcohol and acetone, prepared by Beuchler and Lollar [10] was tested and about 30 per cent of the total epidermis nitrogen was extracted by the procedure and was precipitated in the globular protein fraction with the 3 per cent trichloracetic acid.

Hair or *keratin* is that fibrous material growing from the epidermal lined hair follicles. This material was identified microscopically in the residue.

That these materials, elastic tissue, epidermis, and hair are solubilized very slowly by dilute hydrochloric acid solution, specifically 0.05 N hydrochloric acid, was substantiated by the work of Stubbings [11]. He also used the hydrochloric acid digestion to isolate these materials.

Unextractable globular proteins are those quantities of albumins, globulins and mucoids remaining with the elastic tissue, in the cellular components and in the blood vessels. It is thought by the author that almost complete extraction of these globular proteins occurs when fresh skin is used. It should be made clear at this point that, in this technique, the skin was never allowed to dry out thus avoiding denaturation due to drying. The samples were preserved only a few days in a deep freeze unit, a minimum time necessary to keep them until they could be fractionated. They were sectioned on a freeze ing microtome to avoid the drying necessary to grind them in a mill. Becaus- of this treatment, it was thought that little denaturation occurred. Buechler and Lollar[10] found that they could remove the epidermis by hot water after fast freezing hide samples. This would indicate that little denaturation occurs, because when denaturation does occur, which is the case with salt curing or drying of hide, the epidermis cannot be removed from the hide with hot water.

Analysis of cured stock showed that denaturation of the globular proteins makes them less extractable by the procedure and therefore they remain with the elastic tissue, epidermis and hair fraction, more specifically with the germinating layer of the epidermis.

Fraction II contains the *extractable globular proteins*, those albumins, globulins, and mucoids that are in the solution after the elastin, epidermis and hair are filtered off on glass wool. These proteins are separated from solubilized collagen and non protein nitrogen by precipitation with 3 per cent trichloracetic acid at 85°C.

The globular protein fractions obtained were much greater than those obtained by previous investigators. The reason why previous methods failed to give such results occurred because of the inability to completely remove the globular proteins by the extraction techniques employed. The results are not unreasonable considering the results Roddy[6] obtained with histological techniques. He used a 1 per cent water solution of Gentian Violet to study coagulable proteins and found that in fresh skin in the epidermal area, from the base of the hair roots to the grain surface, there is a concentrated deposition of albumin and globulin, associated particularly with the germinating cells and the erector pili muscles. In the corium the concentration is far less and these proteins are located in the interfibrillary spaces in conjunction with the fibroblasts in their reticular networks; they are also filmed over the collagen fibers. He found that there was a considerable removal of these coagulable proteins by beamhouse processes but even after liming and bating there are some left in the epidermal area of the skin.

Fraction III contains the collagen, that fibrous tissue that is solubilized to gelatin by the 0.1 per cent hydrochloric acid in one hour at 85°C. and is precipitable along with the extractable globular proteins with 30 per cent

trichloracetic acid using bentonite to adsorb the precipitate. Since extractable globular proteins are found in Fraction II, collagen can be determined by difference.

That this collagen determination is correct has been substantiated by work done by the author [12] on many steer hides using the fractionation procedure and by Deasy [13] using the hydroxyproline procedure for determining collagen on many steer hides. The two procedures were proven statistically to give the same results for collagen.

Fraction IV contains the non protein nitrogen which proved to be a very small portion of the skin. It is that nitrogen remaining after the total proteins are precipitated and could consist of amino acids, urea and other nitrogen containing molecules, the building blocks or the waste products of the proteins.

Summary

1. The pretanning operations reduce the elastin-hair-epidermis fraction of calf skin materially.

2. The extractable globular protein nitrogen is also reduced to a small portion of the total nitrogen by the pretanning operations.

3. The non protein nitrogen of the skin changed very little as the result of processing.

4. The purification of collagen was considerable in the pretanning operations. On the calfskin tested the proportion of collagen nitrogen increased from an average of 73.1 per cent to 94.3 per cent.

5. In conclusion it has been shown that processing made considerable change in the protein picture of the calfskin studied and that the fractionation technique has been found to be applicable to the study of protein constituents of skin or hide.

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Factors Affecting the Brine-Curing of Calfskins

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I. INTRODUCTION

The primary objective of curing calfskins is to preserve the inherent desirable characteristics of the skins until they can be manufactured into their ultimate end product. In the case of skins going to the tannery, curing involves preserving the collagenous portions of the skin so that the tanner may produce a durable yet artistic piece of leather. Most calfskins are cured by green salting. Brining of calfskins has not been practiced generally due possibly to a failure to solve some of the problems involved and to a lack of information relative to the weight changes during brining.

Brine-curing not only preserves the skin, but removes moisture, blood and certain non-leather forming proteins. The loss of these substances from the skin usually exceeds the gain in weight due to salt absorption, thus resulting in a net loss in weight, known as the curing shrink. However, the amount of the shrink and in some cases the gain, is affected by a number of factors, which will be discussed in this paper. It will become apparent that the changes during the brining of calfskins are quite dissimilar from those occurring during the brining of hides.

II. LITERATURE

Several researchers (DeBeukelaer and Strandine, 1944, Strandine, et al 1944, Kritzinger 1951) have investigated the brine curing of cattle hides, but very little work has been reported on the use of this method of preservation for calfskins. Stuart and Frey (1934) investigated the effect of various additives to brine as well as the effect of pH of the brines on the bacteriostatic and fungistatic efficiency of the cure. Dempsey et al (1942) reported that brining was a better method than green-salting for curing calfskins. Vourloud and Desjours (1952) reported that various additives to salt had little benefit on the preservation of calfskins.

III. METHODS AND PROCEDURE

In all tests, freshly flayed calfskins were hand-fleshed, the hair clipped, and the skin cut into squares. Usually the whole area of the skin was used except for the shoulder, neck, flanks and shanks. The calfskin pieces were brined at room temperature (70–75°F.) in brines with a weight ratio of 4 parts of brine to 1 part of skin. After brining, pieces were centrifuged for a short time or blotted to remove surface moisture before weighing. In some tests, pieces were analyzed for salt and moisture while the used brines were analyzed for

moisture, salt, pH and extracted protein, both total and coagulable. The pH of brining solutions was not adjusted except in a few controlled experiments, but varied from 7.0 to 7.8 at the start of an experiment and from 6.2 to 6.9 at the end of an experiment.

IV. Results and Observations

1. *Effect of the length of the brining period.*

The average results of brining a light calfskin shown in Figure No. 1,

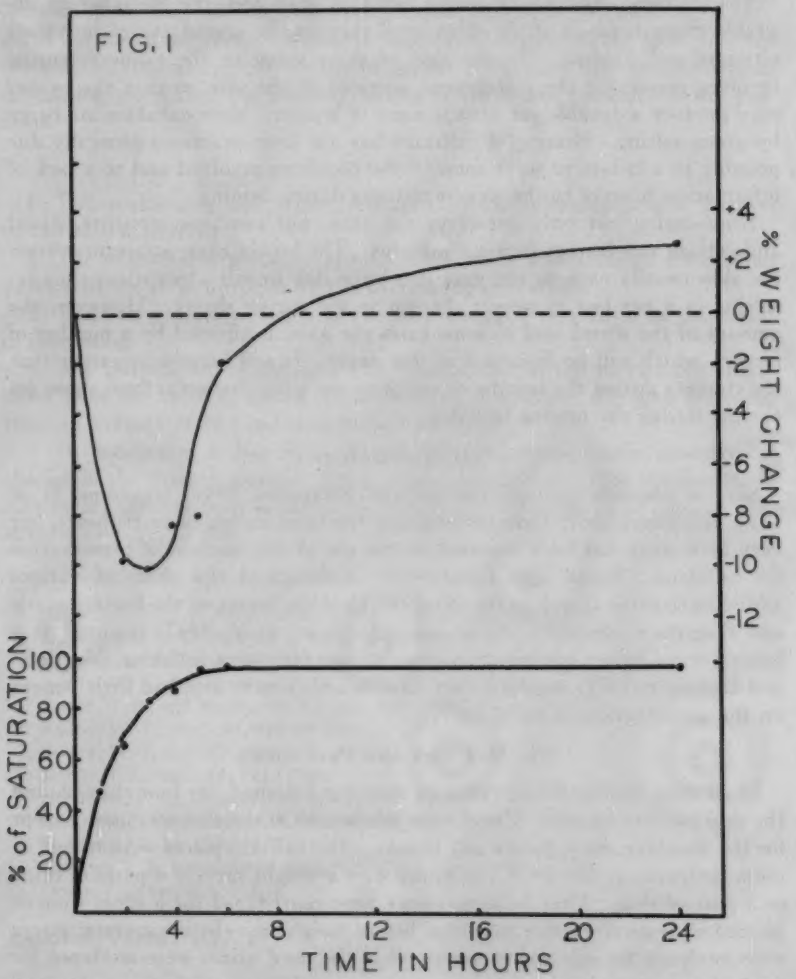

FIGURE 1.—Effect of time on the weight changes and salt absorption of a light calfskin brined in saturated brine.

indicate that during the first hours of brining there is a rapid loss in weight by the calfskin followed by a gradual increase in weight. After a period of time (about 10–24 hours) the brined calfskin equals its own green weight and with continued brining shows a gain in weight in excess of its green weight. Chemical analyses (Table I) show that these changes are due to an initial

TABLE I

Analysis of Brined Pieces of Light Calfskin (7 Lbs.) after Various Periods of Brining

	% H_2O	% Na Cl	% Na Cl Brine	% of Saturation
O Hour	67.8	0.8	1.2	4.5
1 "	57.6	8.5	12.8	48.4
2 "	53.2	11.4	17.6	66.6
3 "	51.2	14.2	21.7	82.2
4 "	51.2	15.3	23.0	87.1
5 "	48.2	16.4	25.4	96.2
6 "	49.0	17.3	26.1	98.8
22 "	51.9	18.2	25.9	98.1

moisture loss from the skin followed by salt absorption and later by absorption of both salt and water. Prolonged brining results in increased hydration and plumping of the calfskins which is reflected in lower shrink figures, a fact which has not been recognized heretofore.

2. *Effect of weight of the skin or the age of the collagen.*

The average change in weight of different calfskins and hides as a function of length of brining is shown in Table 2 and Figures 2 and 3. Figure 2 shows

TABLE 2

Average Weight Changes in Pieces of Skins or Hides after Brining

Length of Brining	Slunk Skin 3½–5 lbs.	Light Calf Skin 6–9 lbs.	Heavy Calf Skin 12–15 lbs.	Kipskin 18 lbs.	Cow Hide 40–50 lbs.	Steer Hide 65–80 lbs.
1 Hour	—11.4%	—10.9%	— 6.0%	— 5.9%	— 7.5%	
2 Hours	— 6.7	—10.8	— 8.6	—10.5	— 8.7	
3 "	— 3.1	—11.3	— 9.7	—13.0	—12.4	— 6.6%
4 "	— 0.9	—10.2	—10.9	—12.3	—11.6	
5 "	+ 8.0	— 9.0	—12.0	—15.6	—12.7	— 7.7
6 "	+ 8.2	— 8.9	—11.3	—15.7		
7 "	+12.2	— 5.0	——	—14.2		
8 "	+12.9					
1 Day	+19.3	+ 0.3	— 9.2	—14.2	—20.5	—19.5
2 Days	+29.3		— 4.5	—11.7	—19.8	—19.8
3 "	+30.6		— 2.5		—18.5	—19.0
4 "	——	+10.7	— 0.3	— 8.1	—15.0	
5 "	+33.3	+11.9	+ 0.7	— 6.7	—13.0	
6 "	+33.6	+15.9	+ 2.3	— 1.3	—14.7	—16.3
7 "	——	+20.5		+ 0.3	—13.3	——
8 "						
9 "			+ 5.1	+12.9		

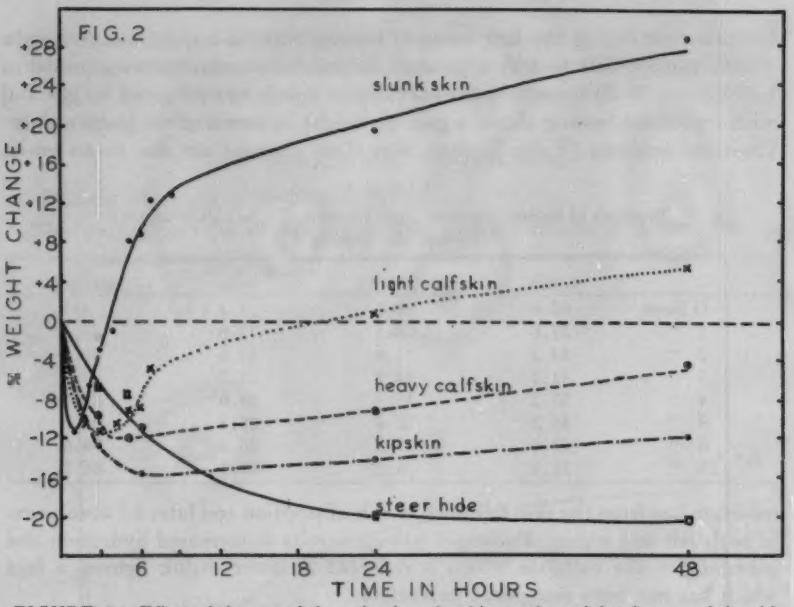

FIGURE 2.—Effect of the age of the animal or the skin on the weight changes of the skin during brining in saturated brine.

the hourly weight changes during the first two days of brining whereas Figure 3 shows the daily weight changes for a whole week of brining.

Examination of Figures 2 and 3 demonstrates that the rate of loss or gain in weight during brining varies according to the weight of the skins. In general, thin light skins are associated with young animals while thicker heavier skins and hides come from older animals. Thus the different weight changes may be related to the thickness of the skin or to the age of the collagen. A slunk skin or very light calfskin loses weight very rapidly but quickly regains its weight so that within four or five hours it may show a gain over its green weight, whereas a kipskin weighing about 18 lbs. loses weight slowly, showing the greatest shrink after 5 to 6 hours of brining and only slowly regaining some weight with continued brining. After a week of brining it shows a slight gain over its green weight. In comparison, a heavy steer hide will show its maximum shrink after 24 to 48 hours brining, will slowly pick up a little weight with continued brining but still will show a shrink of 15–16% after a week of brining. The type of weight-change obtained during brining varies with the kind of skin being brined.

Experiments were conducted to determine if the thickness or the age of the skin were the factor responsible for this brining difference. In the first test a piece of steerhide was split parallel to the grain so that the two pieces

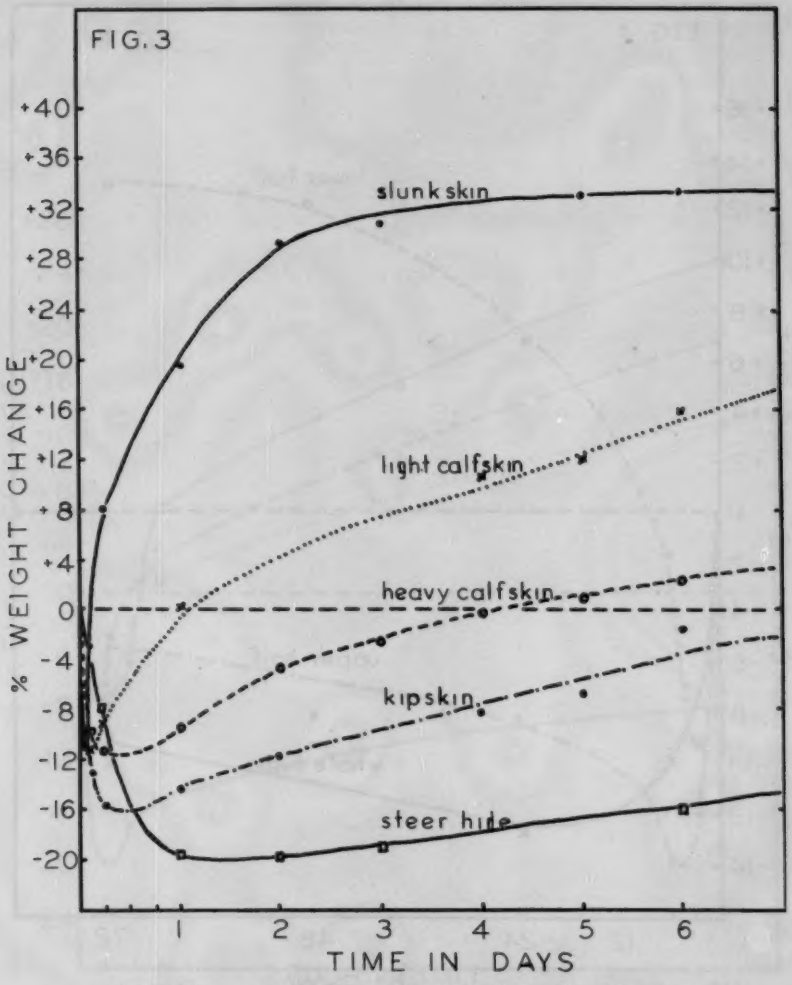

FIGURE 3.—Same as Figure 2 except brining period prolonged.

were about as thick as a calfskin. These were brined and the weight changes recorded. Although both pieces were the same thickness, the two halves had different weight changes during brining. The upper half of the steerhide (Figure 4) had a weight change pattern similar to the whole steerhide while that of the lower half was like that of a calfskin. During growth a calfskin changes into a hide by the addition of collagen fibers to the internal or flesh side of the skin. Thus the flesh side of a hide has the youngest collagen and

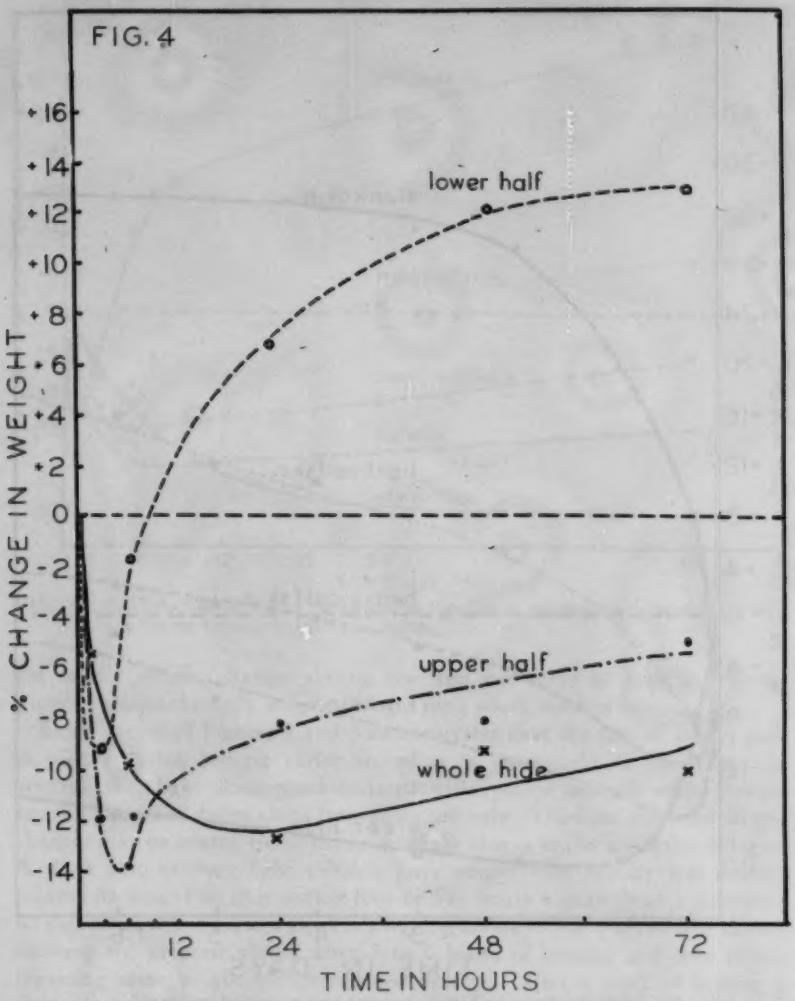

FIGURE 4.—Weight changes during brining in a piece of whole steer hide and in pieces split parallel to the grain surfaces.

should be most similar to the collagen in a young calfskin. The results in this test as well as the next test lend evidence to the hypothesis that it is the age of the collagen and not the thickness of the skin that determines whether it will show a gain or loss on prolonged brining.

In another test, pieces of steerhide were split parallel to the grain into 4 layers about 1.5 millimeters thick. The results of brining are shown in Figure

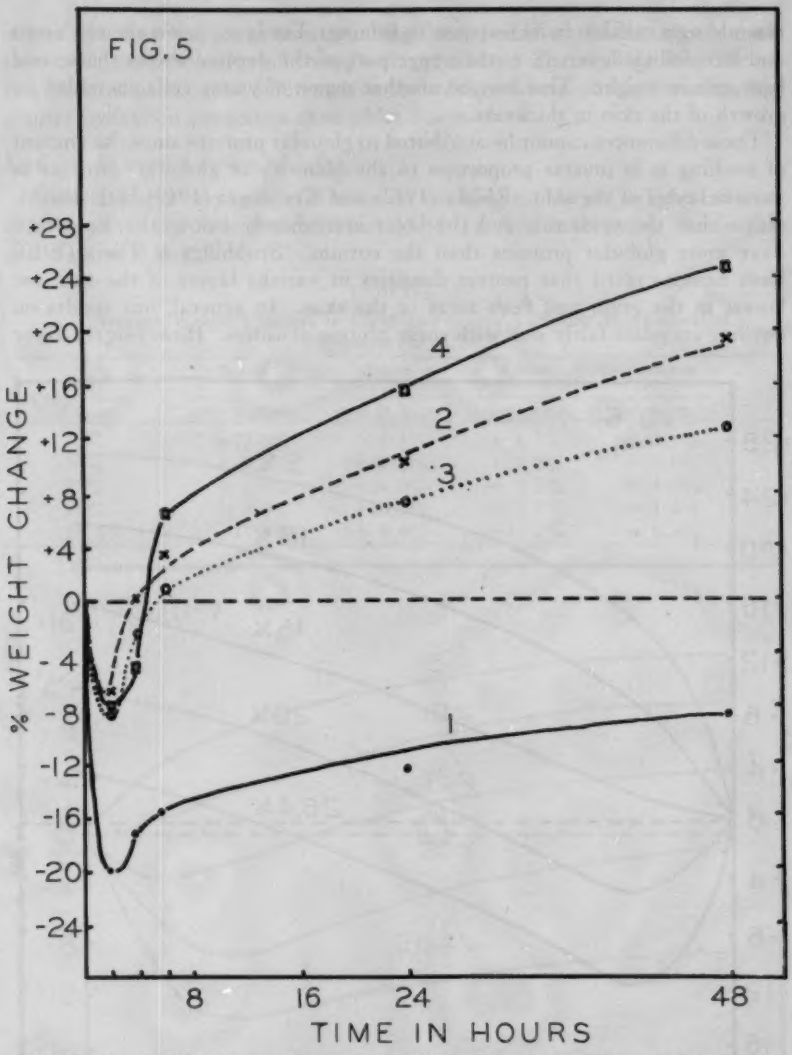

FIGURE 5.—Weight changes during brining in a piece of steerhide split into 4 layers parallel to the grain surface. No. 1 is outside 4th of hide; No. 2 is next to outside layer; No. 3 is next to internal layer; and No. 4 is inner flesh layer.

5 and again indicate that the top hair follicle layer of the hide shows the greatest early shrink during brining and the least regain in weight on subsequent brining. The dermal layer (flesh side) shows the greatest gain in weight

resembling a calfskin in its response to brining. The layer below the epidermis and hair follicle layer, (i. e. the upper part of the dermis) shows the second best gain in weight. This may be another region of young collagen added by growth of the skin in thickness.

These differences cannot be attributed to globular proteins since the amount of swelling is in inverse proportion to the quantity of globular proteins in various layers of the skin. Roddy (1942) and Kritzinger (1949) both demonstrate that the epidermis and the layer immediately below the epidermis have more globular proteins than the corium. Stubbings & Theis (1950) have demonstrated that protein densities in various layers of the skin are lowest in the grain and flesh areas of the skin. In general, our results on swelling correlate fairly well with these protein densities. However, the layer

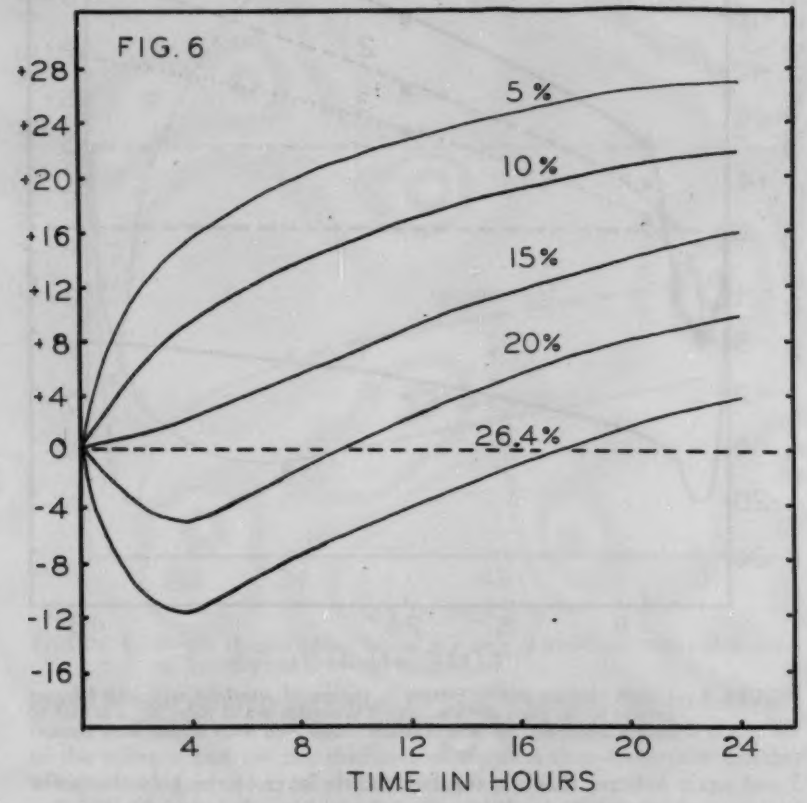

FIGURE 6.—Hourly weight changes in *light* calfskin brined in various concentrations of brine.

nearest the flesh has the greatest swelling due possibly to the fact that it contains a higher percentage of young collagen fibers. The swelling may therefore be attributed to the differences in the collagen fibers, young fibers having greater hydration properties than older fibers.

3. *Effect of concentration of brine.*

The effect of concentration of brine on the weight changes in light calfskin (7¼ lbs. Av.) and in heavy calfskins (15 ¼ lbs. Av.) is shown in Table III and Figures 6 and 7.

TABLE 3

Average Weight Changes in Light and Heavy Calfskins as Affected By Concentration of Brine

Concentration of Brine	In Light Weight Calfskins (7¼ lbs. Av.)		In Heavy Weight Calfskins (15¾ lbs. Av.)	
	After 4 Hours	After 24 Hours	After 4 Hours	After 24 Hours
5%	+15.5%	+26.3%	+ 6.7%	+13.1%
10%	+ 9.4%	+22.1%	+ 2.2%	+10.0%
15%	+ 1.9%	+16.0%	— 2.7%	+ 4.6%
20%	— 5.0%	+10.1%	— 7.7%	— 1.3%
26.4%	—11.8%	+ 4.0%	—13.2%	— 8.8%

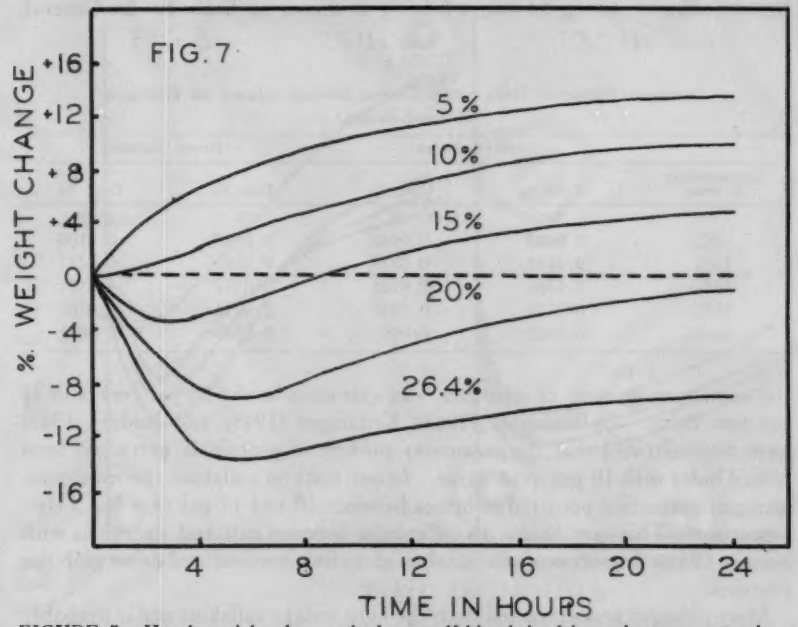

FIGURE 7.—Hourly weight changes in *heavy* calfskins brined in various concentrations of brine.

When brined in 5 or 10 per cent NaCl solution, both the light and the heavy calfskins absorb brine and show a rapid increase in weight. In more concentrated brines the early weight changes are losses while later the weight changes reverse to a gain. The more concentrated the brine the more rapid is the early shrink in brining and the slower is the regain in weight.

The degree of salt saturation in the light and heavy calfskins after 24 hours brining is directly related to the concentration of brine used (Table 4).

TABLE 4

Analysis of Brined Calfskins

	Brined Light Calfskins			Brined Heavy Calfskins		
Concentration of Brine Used	% Na Cl	% H_2O	% of Saturation	% Na Cl	% H_2O	% of Saturation
5%	3.7	70.4	18.9	3.3	66.8	17.7
10%	7.1	66.7	36.4	6.3	62.7	34.3
15%	10.5	62.2	54.5	9.4	58.6	52.2
20%	12.8	58.2	68.2	11.9	54.0	68.3
26.4%	17.6	51.3	96.9	15.8	47.9	93.6

The amount of both total and coagulable nitrogen extracted from light and heavy calfskins during 24 hours brining is shown in Table 5. In General,

TABLE 5

Nitrogen Extracted from Skins During Brining (Based on Nitrogen in Used Brines)

	Light Calfskins		Heavy Calfskins	
Concentration of Brine	Total N_1	Coag. N_2	Total N_1	Coag. N_2
	%	%	%	%
5%	0.0403	0.0042	0.0348	0.0100
10%	0.0413	0.0139	0.0351	0.0131
15%	0.0386	0.0141	0.0352	0.0131
20%	0.0378	0.0132	0.0294	0.0105
26.4%	0.0262	0.0095	0.0249	0.0081

the maximum amount of nitrogen was extracted in the 10 per cent and 15 per cent brine. DeBeukelaer (1944), Kritzinger (1948) and Roddy (1942) have demonstrated that the maximum amount of protein is extracted from brined hides with 10 per cent brine. In our tests on calfskins the maximum nitrogen extraction occurred in brines between 10 and 15 per cent NaCl concentration. This may be due to differences between calf and steerhides with respect to the proportions of albumins, globulins, mucins, and other globular proteins.

More nitrogen was extracted from the light weight calfskins and is probably due to the fact that younger skins contain more soluble globular proteins.

McLaughlin and Theis (1924) demonstrated that calfskins contained 5.1 per cent albumen and globulins while steerhides had 1.9 per cent.

4. *Effect of the ratio of brine to skin weight.*

Pieces of light and heavy calfskins were clipped and then brined in saturated brine, the ratio of the weight of brine to skin being 2:1, 4:1 and 8:1. The effect of not clipping the hair was also investigated. Weight changes were recorded and are shown in Table 6 and in Figure 8.

TABLE 6

Effect of the Ratio of Weight of Brine to Skin on the Shrink of Brined Calfskins

Hair Clipped	Ratio of Brine to Skin	Av. Shrink in Light Calfskins (7½ lbs.)		Av. Shrink in Heavy Calfskins (13½ lbs.)	
		After 4 Hours	After 24 Hours	After 4 Hours	After 24 Hours
		%	%	%	%
Yes	2:1	— 7.9%	+ 4.6%	—11.6%	— 6.1%
Yes	4:1	— 9.4	+ 5.1	—12.8	— 6.5
Yes	8:1	—11.7%	+ 6.3%	—13.8	— 7.2
No	4:1	— 3.6%	+14.4	—10.7	— 3.3

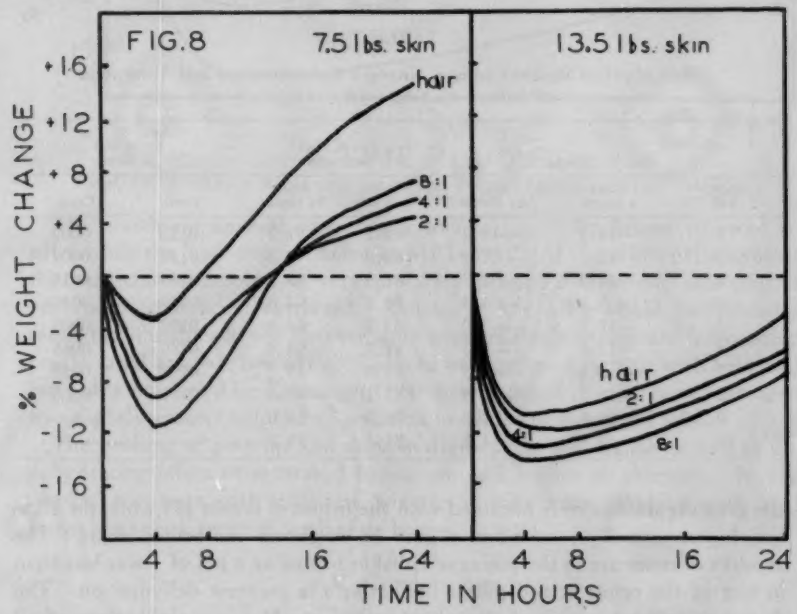

FIGURE 8.—Effect of hair and the ratio of brine to skin weight on the weight changes of brined light and heavy calfskins.

In light calfskins the shrinks after 4 hours brining as well as the gains after 24 hours brining were greater in the 8:1 brine ratio than in either the 4:1 or 2:1 ratios. The piece with unclipped hair did not shrink as much after 4 hours brining and showed a greater gain after 24 hours brining, due no doubt to the hair absorbing large quantities of brine.

In the case of the heavy calfskins, the greatest shrinks were obtained with the 8:1 ratio of brine to skin weight. The pieces with hair did not show as great a shrink after either 4 hours or 24 hours brining. The absorption of brine by the hair is a factor which influences the shrink or gain of a calfskin during brining and subsequent storage.

5. *Effect of pH of brine.*

In studying the effect of pH, calfskins weighing 10.5 to 11.5 lbs. were clipped, fleshed, cut into squares and brined in saturated brines in which the pH was adjusted with HCl or NaOH. The pH was tested and re-adjusted repeatedly during the first 4 hours of brining after which there was very little further change in the pH. Brines were adjusted from pH 1 to pH 10.

Examination of Table 7 and Figure 9 indicates that after 24 hours brining

TABLE 7

Effect of pH on Weight Changes, Nitrogen Extraction and Salt Absorption of Brined Calfskins (Av. 11 Lbs.)

	Av. % Shrink		Av. % Salt Saturation		Av. % N_2 Extracted in Brine	
pH	After 4 Hours	After 24 Hours	After 4 Hours	After 24 Hours	Total	Coag.
1	—14.7	—11.2	81.2	97.7	.0126	.0002
2	—11.1	— 5.2	82.0	93.2	.0127	.0009
3	—10.2	— 2.7	81.5	95.8	.0145	.0018
4	— 9.2	— 3.3	80.5	94.6	.0147	.0030
5	—11.1	— 3.0	82.2	94.8	.0198	.0069
6	—12.5	— 1.4	81.7	94.5	.0189	.0065
7	—10.8	— 0.5	81.9	95.2	.0188	.0058
8	—11.4	+ 1.6	83.1	95.5	.0179	.0066
9	—11.2	+ 3.9	78.3	94.0	——	——
10	— 9.8	+ 4.2	81.4	95.5	——	——

the greatest shrinks were obtained with the brines of lowest pH while the alkaline brines actually resulted in a gain in weight of the brined skins. The amount of moisture in the pieces of calfskin brined at a pH of 1 was less than in any of the other brined pieces indicating the greatest dehydration. The degree of salt saturation of the pieces brined at pH 1 was the highest of all the pieces, but was only slightly higher than in the pieces brined at the other pHs.

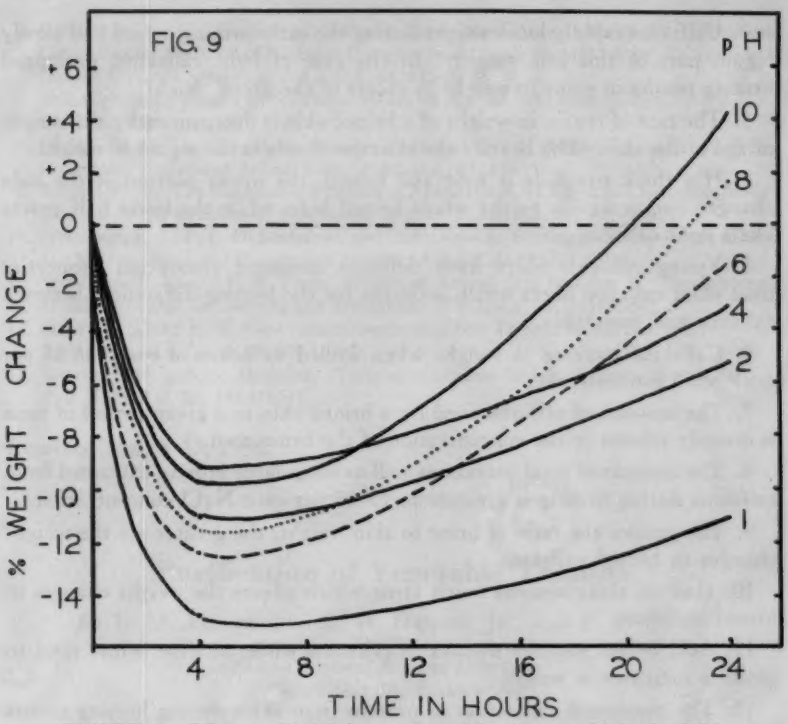

FIGURE 9.—Effect of pH of brine on the weight changes of brined calfskin.

The maximum amount of nitrogen was extracted by brines adjusted to pH 5 while the least was extracted at pH 1 and 2. At these low pH's some of the extractable nitrogen is very probably precipitated in the skin and is prevented from being extracted. Curing at low pH's would undoubtedly result in difficulties at the tannery since some of the proteins are irreversibly precipitated at these low pH's. Reduced extraction of protein with brines of low pH is supported by Kritzinger (1948A) who found that extracted nitrogen was slightly greater at pH 3.05 and was much lower below pH 3.05.

The swelling of proteins and skins in dilute acids and alkalis as well as the dehydrating effect of saturated brines are well known to chemists. In the case of our tests with calfskins, greater shrinks were obtained with acid brines than with neutral or alkaline brines.

V. Conclusions

1. Weight changes in calfskins during brining are quite different than those in heavy cow or steerhides.

2. Calfskins rapidly loose weight during the early brining period and slowly regain part of this lost weight. In the case of light calfskins, prolonged brining results in gains in weight in excess of the green weight.

3. The rate of regain in weight of a brined skin is determined by the weight or age of the skin. The heavier the skin the slower is the regain in weight.

4. If a thick steerhide is split and brined, the upper portion of the hide changes weight similar to the whole brined hide, while the lower half reacts like a light calfskin.

5. Young collagen fibers have different moisture absorption properties than older collagen fibers which accounts for the brining differences between calfskin and steerhides.

6. Calfskins increase in weight when brined in brines of less than 15 per cent NaCl concentration.

7. The amount of salt absorbed by a brined skin in a given period of time is directly related to the concentration of the brine used.

8. The amount of total protein as well as coagulable protein extracted from calfskins during brining is greatest in 10–15 per cent NaCl concentration.

9. The greater the ratio of brine to skin weight, the greater are the weight changes in brined calfskins.

10. Hair on skins absorbs much brine which affects the weight changes in brined calfskins.

11. Acid brines produce shrinks in calfskins while alkaline brines tend to produce increases in weight.

12. The maximum extraction of protein from skins during brining occurs in brines of pH 5 to 7.

13. For successful commercial brining of calfskins certain precautions will be necessary relative to the average weight of skins, the concentration of brine, pH of brine, ratio of brine to skin weight, length of brining and draining and storage conditions. Exact procedures will have to be determined by the needs and requirements of each producer of cured calfskins.

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Purification of Vegetable Tannins

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It has been clearly demonstrated recently that vegetable tanning extracts are complex mixtures of tannins and non-tannins [1]. In the study of the physical and chemical properties of these naturally occurring vegetable tannins, it is important to obtain the tannins in a high state of purity. Various general methods for purifying the tannins have been previously employed [2, 6]. These methods include: (1) Adsorption of tannins by hide powder, (2) Precipitation of the tannins with lead acetate, (3) Salting out of aqueous solution by sodium chloride, and (4) Purification through the use of various organic solvents.

The use of organic solvents for purifying the vegetable tannins appears to merit investigation for developing a satisfactory method for obtaining tannins in a high state of purity. Previous workers have employed organic solvents for this purpose, but in general the results have been highly empirical and it has been necessary to resort to mixtures of solvents to accomplish this purpose [5, 6]. More suitable organic solvents for purifying tannins are needed. Because of certain properties methyl ethyl ketone seemed to merit investigation.

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Methyl ethyl ketone is partially miscible with water; and the properties of methyl ethyl ketone-water mixtures, particularly the fact that this ketone at equilibrium dissolves water to the extent of 12.6% by weight, suggested that this solvent may be generally useful for purifying vegetable tannins. The results of such an investigation are reported in this paper.

Experimental

The crude canaigre extract was obtained by batchwise leaching of canaigre roots with a 50% acetone-water solution as described previously [7]. Tannic acid was obtained by leaching Chinese gall nuts with water. The other extracts studied were the commercially available extracts.

Purification by Liquid-Liquid Extraction with Methyl Ethyl Ketone

The procedure described below is typical of the method used for purifying the various extracts. The crude, dry extract was dissolved in water to give solutions of 25% by weight (solids content). The aqueous solution was extracted in a separatory funnel five times with methyl ethyl ketone which had previously been saturated with water. The volume ratio of solvent to aqueous liquor was 1.0 for the first extraction and 0.5 for subsequent extractions. The methyl ethyl ketone layers were combined and evaporated to dryness in a vacuum still heated by steam, the final stage of drying being carried out at a pressure of approximately 1.0 mm of mercury. The residual solid was ground, and the tannin content determined by the Official Method of the American Leather Chemists Association [8].

In a few cases difficulty in separating the two liquid phases was encountered in the first stage of extraction. This difficulty was generally overcome by filtering the mixture through a small plug of cotton or by centrifuging the mixture. In the case of quebracho extract the insolubles which separated from the hot aqueous solution on cooling were removed by decantation prior to extraction with methyl ethyl ketone.

The results obtained in the purification of aqueous solutions of various tannins with methyl ethyl ketone saturated with water are shown in Table I. In the case of canaigre tannin substantially the same results were obtained whether dilute solutions, 10% solids liquor, or more concentrated solutions, 50% solids or the solid extract, were used. The results obtained with other solvents are shown in Table II. Considerable difficulty in separating the two liquid layers was encountered in the extractions using methyl isobutyl ketone as the solvent.

The "apparent" distribution of canaigre tannin between water and methyl ethyl ketone was determined as follows: equal volumes of an aqueous solution of the tannin and water saturated ketone were shaken, the organic layer separated and the solvent evaporated. The solid extract was analyzed for

TABLE I

Purification of Tannins by Liquid—Liquid Extraction with Methyl Ethyl Ketone

Tannin	Analysis of Extract %												
	Crude Extract						Refined Extract						
	Total solid	Soluble solid	Insol.	Non Tannin	Tannin	Purity*	Total solid	Soluble solid	Insol.	Non Tannin	Tannin	Purity*	Tannin Recovery %
Canaigre†	94.5	94.4	0.1	47.1	47.3	50.1	87.7	87.7	0.0	8.5	79.2	90.3	88
Wattle bark	91.1	88.9	2.2	23.1	65.8	74.0	100.2	99.5	0.7	5.7	93.8	94.2	65
Quebracho	86.5	80.7	5.8	7.9	72.8	90.2	96.0	92.7	3.3	4.4	88.3	95.3	58
Sulfited quebracho	92.0	91.5	0.5	15.7	75.8	82.9	96.5	95.4	1.1	6.7	88.7	93.0	56
Myrobalans	95.0	91.6	3.4	33.0	58.6	64.0	96.7	95.7	1.0	11.4	84.3	88.1	79
Tannic acid	97.8	96.0	1.8	14.5	81.5	84.9	96.5	94.5	2.0	8.0	86.4	91.6	90
Divi Divi‡	25.7	24.2	1.5	12.6	11.6	47.9	96.6	92.9	3.7	18.1	74.7	80.5	68
Cube Gambier	90.8	49.7	41.1	32.0	17.7	35.6	98.1	93.5	4.6	29.7	63.8	68.2	97
Plantation Gambier	92.4	85.7	6.7	37.1	48.6	56.7	88.6	84.5	4.1	26.1	58.4	69.1	80
Hemlock bark‡	27.9	27.5	0.4	7.3	20.2	73.6	94.3	86.9	7.4	10.3	76.6	88.1	39
Valonia	91.0	89.5	1.5	25.6	63.9	71.4	97.6	84.6	13.0	18.9	65.7	77.7	15
Chestnut	92.5	91.7	0.8	29.8	61.9	67.5	96.9	93.8	3.1	24.9	68.9	73.4	20
Borneo cutch	76.1	73.6	2.5	16.8	56.8	77.2	97.4	92.0	5.4	9.0	83.0	90.2	18
Mangrove bark	88.3	87.9	0.4	21.8	66.1	75.2							<8

*Purity = % Tannin/% Sol. solids x 100.
†a 50% solids content liquor was extracted. Total sugar (as glucose): in crude, 36.4%; in refined, 4.3%.
‡analysis of the crude based on a 25° Twaddell liquor.

tannin content and the "apparent" distribution calculated. The results are shown in Table III.

TABLE II

Purification of Tannins with Other Organic Solvents*

Tannin	Solvent	Purity ** % Crude	Purity ** % Refined	Tannin recovery, %
Canaigre	Sec. –Butyl alcohol	47.7	68.4†	67
Canaigre	tert. Amyl alcohol	50.1	74.8‡	52
Canaigre	Methyl isobutyl Ketone	47.7	90.6	33
Tannic acid	" " "	84.9	93.2	85
Plantation Gambier	" " "	56.7	66.0	53
Wattle	" " "	74.0	90.8	18
Myrobalans	" " "	64.0	87.6	22
Divi Divi	" " "	54.6	70.8	17
Cube Gambier	" " "	35.6	59.8	47
Quebracho	" " "	90.2	93.5	29
Sulfited quebracho	" " "	82.9	93.9	25
Chestnut	" " "	67.5	57.8	7

* Extraction of liquors from Mangrove, Valonia and Borneo cutch with Methyl isobutyl ketone resulted in very low tannin recovery (<4%).

**Purity = $\frac{\%\ \text{tannin}}{\%\ \text{Sol. solid.}} \times 100$

†Total sugar (as glucose): in crude, 37.4%; in refined, 20.3%.

‡Total sugar (as glucose): in crude, 36.4%; in refined, 16.4%.

TABLE III

Apparent Distribution of Canaigre Tannin between Methyl Ethyl Ketone (MEK) and Water

Treatment	Phase, ml. H_2O	Phase, ml. MEK	Solid in MEK, g.	Tannin %	Purity %	K=Ca/Cw*	Extraction eff., %†
10% Canaigre‡—1st extraction	550	270	14.5	90.6	93.2	4.05	66.5
2nd extraction	555	550	4.1	82.1	84.0	1.37	17.1
3rd extraction	550	535	1.2	—	—	—	—
25% Canaigre‡—1st extraction	174	131	17.8	90.6	91.3	5.95	81.8
2nd extraction	174	170	2.1	76.1	78.6	0.82	8.1
50% Canaigre‡—1st extraction	55	82	21.2	84.5	84.9	6.25	90.8
2nd extraction	56	47	0.9	—	—	—	—

*On tannin content basis; Cs = concentration of tannin (g/ml), as determined by hide powder, in MEK phase; Cw = concentration of tannin (g/ml.) in H_2O phase (by difference).

†Extraction efficiency = tannin in MEK/total tannin in crude X 100.

‡Analysis of solid crude canaigre: TS, 96.7; SS, 96.8; Tan., 46.1; Non-tan., 50.7; purity, 47.7. In each case the aqueous solution contained 42.8 g. of solid extract.

Leaching of Tannins from Plants with Methyl Ethyl Ketone-Water Azeotrope

The finely divided plant material, 25 to 50 g., was placed in the thimble of a Soxhlet apparatus. A mixture of methyl ethyl ketone and water (generally 250 ml. of ketone and 75 ml. of water) was refluxed in the still pot of the

Soxhlet, and the semi-continuous leaching of the plant source of tannin was continued until extraction appeared complete (10 to 20 hours). Both the solvent and aqueous layers in the still pot were transferred to a vacuum still heated by steam where solvent and water were evaporated, the final stages of drying being conducted at a pressure of approximately 1 mm. of mercury. The residual solid was ground and analyzed according to the Official Method of the ALCA. The results are shown in Table IV. In the case of canaigre

TABLE IV

Leaching of Tannins from Plant Source with Methyl Ethyl Ketone—Water Azeotrope

Tannin Source	Tannin recovery, %	Analysis of Extract, %					
		Total solids	Soluble solids	Ins.	Non-Tannin	Tannin	Purity*
Sumac leaves (Sicilian)	96	48.9**	41.5**	7.4**	9.5**	32.0**	77.2
Gallnuts (Chinese)	88	91.9	89.4	2.5	8.8	80.6	90.1
Canaigre roots (shredded)	69	97.6	93.7	3.9	23.7	70.0	74.7
Canaigre roots (powdered)†	46	93.6	89.6	4.0	7.8	81.7	91.3
Canaigre roots (powdered)‡	80	96.3	90.2	6.1	6.9	83.3	92.3
Wattle bark	87	93.6	88.5	5.1	9.3	79.3	89.5
Hemlock bark	82	97.2	76.4	20.8	23.0	53.4	69.9

*Purity $= \frac{\%\text{tannin}}{\%\text{ sol. solid}} \times 100$

**The tannin was obtained in aqueous medium

†Leaching appeared to occur mainly at the outer portion of the canaigre root mass.

‡Leaching conducted in vacuum, Soxhlet apparatus maintained at a pressure of 250–350 mm. of Hg.; temperature of the refluxing methyl ethyl ketone–water azeotrope was 50 to 53° C.

better results were obtained when the leaching was conducted at reduced pressure (250 – 350 mm.), the boiling point of the methyl ethyl ketone-water azeotrope being reduced from 73° C. to approximately 50–55° C.

Discussion

Methyl ethyl ketone is a relatively low-cost, commercially available organic solvent which is partially miscible with water. At room temperature the solvent layer of the two phase system of methyl ethyl ketone and water contains 12.6% by weight of water and 87.4% by weight of methyl ethyl ketone [9]. Thus it would appear that this solvent may be of value for purifying tannins by liquid-liquid extraction of aqueous tannin solutions, and such was found to be the case. Because of the low tannin recoveries this solvent was not useful with valonia, chestnut, Borneo cutch, and mangrove extracts. The purity of all the vegetable tannins investigated, excepting mangrove bark extract, was considerably improved. Extracts of purity ranging from 88 to 95% were obtained in the batchwise liquid-liquid extraction of quebracho, sulfited quebracho, wattle, canaigre, myrobalans, tannic acid, and hemlock tannins. The purity of the extracts was not quite so high, approximately

70–80%, when this method of purification was applied to divi-divi and gambier extracts. Recovery of tannin amounted to 80% or better in the case of canaigre, myrobalans, tannic acid, cube gambier, and plantation gambier. Tannin recoveries in the range of 40 to 65% were obtained with wattle, quebracho, sulfited quebracho, and hemlock bark extracts. It would be expected that higher extraction efficiency would result from continuous countercurrent liquid-liquid extraction than from batchwise extraction. The use of methyl isobutyl ketone in place of methyl ethyl ketone gave satisfactory results only in the case of tannic acid, from which 85% of the tannin was recovered in a state of purity of 93%. In general, excepting tannic acid and the gambiers, very low tannin recoveries were observed using methyl isobutyl ketone as a solvent in liquid-liquid extraction, and this solvent does not appear to be as promising as methyl ethyl ketone for purifying the tannins. Secondary butyl alcohol and tertiary amyl alcohol, which are also partially miscible with water, were considerably less selective and efficient than methyl ethyl ketone in purifying canaigre tannin. From data obtained with canaigre extract it appears that methyl ethyl ketone, saturated with water, is a highly selective solvent for separating sugars from certain tannins.

That methyl ethyl ketone saturated with water is an effective solvent, at least for canaigre tannin, is indicated by the data in Table III. Thus, in the distribution of this tannin between water and methyl ethyl ketone the solvent phase is considerably richer (approximately five fold) in tannin than the aqueous phase. In extracting concentrated aqueous solutions of canaigre tannin, one extraction suffices to remove 90% of the tannin in a high state of purity. The sugar and ash content of canaigre tannin, originally 36.4% and 4-5%, respectively, were reduced to 4.3% and 0.3% respectively by liquid-liquid extraction of the aqueous crude tannin with methyl ethyl ketone.

Methyl ethyl ketone forms an azeotrope, or constant boiling mixture, with water boiling at 73.4°C., which is very easily recovered by distillation of aqueous systems of this ketone. The azeotrope is composed of 88.7% by weight of methyl ethyl ketone and 11.3% by weight of water [9]. Thus the composition of the azeotrope is almost identical to the composition of methyl ethyl ketone saturated with water. It therefore appeared likely that this azeotrope could be satisfactorily used to leach tannins from the plant source, in a semi-continuous operation such as in a Soxhlet extractor, and perhaps give simultaneously both high purity and tannin recovery. The results in Table IV show that this was accomplished in the leaching of Chinese gallnuts, canaigre roots, and wattle bark with this azeotrope. Extracts of approximately 90% purity were obtained with extraction efficiencies ranging from 80–88%. Leaching of sumac leaves, although resulting in high tannin recovery, gave an extract of only 77% purity. Somewhat similar results were obtained with hemlock bark. Satisfactory leaching of canaigre roots by this method was

only possible by conducting the process at reduced pressure (azeotrope boiled at approximately 50° C.), probably because gelatinization of the starch in the roots occurred when operated at atmospheric pressure (boiling point of azeotrope 73° C.). It is interesting to compare the leaching of wattle bark (Table IV.) and the liquid-liquid extraction of aqeous solution of wattle tannin (Table I.), with this aqeous ketone. In the former case a considerably higher tannin recovery was obtained with but a slight lowering of purity of the extract. This is in contrast to the case of hemlock bark tannin, where improved extraction efficiency is accompanied by considerably lower purity.

Summary

Methyl ethyl ketone saturated with water appears to be an example of a single organic solvent generally useful for purifying tannins. Tannins ranging from 88 to 95% purity were obtained by liquid-liquid extraction of aqeous solutions of tannins from wattle, hemlock, canaigre, quebracho, sulfited quebracho, myrobalans and gallnuts. Extracts of 70 to 80% purity were obtained from divi-divi and cube and plantation gambier.

High tannin recovery (80 to 97%) was observed in the case of canaigre, myrobalans, tannic acid, and cube and plantation gambier. Tannin recovery amounting to 40–65% resulted from wattle, quebracho, sulfited quebracho, divi-divi, and hemlock tannins. Low tannin recovery (below 20%) was observed in the case of valonia, chestnut, Borneo cutch, and mangrove extracts.

The use of methyl ethyl ketone-water azeotrope to leach tannin from sumac leaves, hemlock bark, canaigre roots, wattle bark and Chinese gallnuts (in a Soxhlet extractor) was found to give satisfactory extraction in the latter three instances, and moderately good results in the first two instances. Thus equilibrium systems of methyl ethyl ketone and water appear to have some value in purifying certain vegetable tannins.

Acknowledgment

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ABSTRACTS

The Influence of the Conditions of Storage and of the Composition of Pickle Liquor on the Deterioration of Skins. J. H. Bowes and R. G. Mitton. *J. Soc. Leather Trades' Chemists*, **39,** 36 (1955). Sheepskins in large numbers are preserved for storage and transporation by pickling in solutions of NaCl and H_2SO_4. Since damage is sometimes found, it would seem that careful control may be necessary. Previous investigations provided little quantitative information regarding extent of degradation except under extreme conditions and they did not show whether, when the best pickle was used, steady and progressive deterioration took place during prolonged storage. In a laboratory experiment, described in detail, pelt samples were pickled with 3, 6, 12 and 24 per cent salt and 0.75, 1.50, 2.25 and 3 per cent sulfuric acid, on the limed weight. After removal of the sample the pickle liquors contained respectively 0.003, 0.026, 0.119 and 0.240 *N* acid. Samples were stored at 0, 20, 30 and 40 degrees C. for various periods up to nine months and assessed therafter in various ways for deterioration. The influence of fat content of the pelt, and of iron and calcium ion concentrations was also studied. Although dusted with mold spores before storage, none grew much mold. Deterioration was chiefly due to chemical action. The results show that there is no method of pickling with salt and sulfuric acid which avoids deterioration entirely. Irrespective of whether the damage is assesed by soluble nitrogen determination, shrinkage temperature, or the strength of leather made from the pelt, storage in pickle always results in progressive deterioration at a rate which decreases with time, but is still appreciable after nine months storage. If the storage temperature can be kept below 20°C., damage is relatively slight. At such low temperatures the amount of damage is little altered by acid or salt concentration changes, in the ranges used, although it increases steadily with the amount of acid. At higher temperatures damage becomes severe, especially at higher acid concentrations. Fairly high salt concentration is advantageous in these circumstances and the production of nitrogen is least at the highest salt concentration. However, from strength of leather and shrinkage temperatures, there is some evidence that a salt concentration near 12 is better than 24 per cent salt. The present investigation shows that the acid concentrations usually recommended are dangerous, if storage is at above 30°C. even for short periods. If temperatures around 40°C. cannot be avoided, the acid in the pickle should not exceed 0.025 *N*, or at most 0.1 *N* (0.5 per cent). Unfortunately such low acid content seems to be precluded in practice by the necessity of avoiding mold. Small quantities of iron or calcium in the pickle liquor caused no loss of strength: but samples which contained fat during the pickling and storage gave somewhat weaker leather than the fat free ones, although the fat was removed before tannage. Comparison of results of strength tests and soluble nitrogen determinations indicate that

the latter provides a good measure of the extent to which deterioration has influenced the physical properties of the pelt. Shrinkage temperatures and strength tests also run parallel: but, since shrinkage temperatures are influenced by other processes (e.g. liming), they may be less reliable. The pH values of water extracts from pickled pelts rise with increasing duration of storage and such measurements are consequently unsatisfactory criteria of the acid concentration of the original pickle. R.H.T.

Chromium Fixation on Acetylated Collagen. R. L. Sykes. *J. Soc. Leather Trades' Chemists*, **39**, 56 (1955). Merino sheepskin, which had been limed, delimed, bated and thoroughly degreased was used as the source of collagen. N-acetylation was effected with 5 per cent acetic anhydride in acetic acid continuously agitated for 12 hours. O and N-acetylation were with 50 per cent acetic anhydride in acetic acid for 10 days. Collagen was esterified with catalyzed methanol and then acetylated as above. Also a sample was esterified after O- and N-acetylation. Chromic sulfate solution with basicity adjusted with NaOH and diluted to 25.3 g. per liter and aged 3 months was used for tanning. Two gram samples were tanned in a shake machine at 60 r.p.m. for 48 hours. Curves are plotted showing per cent of Cr_2O_3 on collagen versus percent basicity, also shrinkage temperatures versus per cent basicity, for normal collagen and all the modified collagens. Although acetylation brought about a reduction of the chromium fixed, it did not affect the shrinkage temperature. On the other hand esterification causes a reduction in both chromium fixation and hydrothermal stability. The results give no indication that groups, other than the carboxyl, are involved in the reaction producing hydrothermal stability. They confirm that chromium combines with hydroxyl residues to form a product sufficiently stable to stand washing. This reaction may be assumed to involve residual valency or hydrogen bonding. The conclusion is that cationic chrome tannage involving carboxyl groups confers hydrothermal stability. The same tannage involving hydroxyl groups does not increase the hydrothermal stability and is of minor importance in normal chrome sulfate tannage. R.H.T.

Fundamentals of the Chemistry of Synthetic Dyestuffs and Their Application in Leather. By J. K. De. *Tanner*, **8**, No. 6, 23, No. 7, 15 (1953). The author classifies dyes as acid, basic and direct, and specifies their method of application and the finishing of the dyed product. Thus acid dyes are suitable for all classes of leathers — basic for vegetable and mordanted chrome, and direct for chrome and alum leathers. All leathers need to be finished by rinsing in water and subsequently fatliquored after the dyeing. The author applies the law of parallelogram of forces to the blending of two dyes of primary color to arrive at a third color. The law is stated as follows: if the component colors, not exceeding two in number are arranged in the order of the color of the solar spectrum in a cyclic fashion, the colors being represented in intensity and shade by two adjacent sides of a parallelogram obtained by drawing lines through the center, the resultant color will be represented in shade and intensity by the diagonal of the parallelogram passing through the center. Thus a mixture of red and yellow dyes of nearly equal tinctorial strength in equal proportions, as represented by the arms of the parallelogram, will give an orange. The author illustrates the foregoing by diagram. Other diagrams are shown to illustrate other mixtures of two or more colors. When black is mixed with one or two colors within the color range of the spectrum, altogether different results are obtained which cannot be deduced from the above simple rules.

Some Aspects of Leather Science. By Y. Nayudamma. *Tanner*, **8**, No. 8, 23 (1954). A lecture on hide as a raw material, its preservation, soaking, liming, deliming, bating and pickling. The author mentions the production of Nari leather on a cottage scale, where the milk of akand leaves has been used for ages in place of liming, deliming and bating of skins.

The milk contains certain proteolytic enzymes which bring about the desired effect of unhairing and bating. A description of vegetable, chrome, and aldehyde tannages follows. Modernization of plant and equipment is recognized as a necessity in this day of streamlined production. From ancient times tanning has been an important Indian industry and, while it is recognized as one of major economic importance to India, it remains with few exceptions a cottage industry with craftsmanship based more on empirical knowledge than on scientific principles. With the production of 58 million hides and skins annually, the scientific exploitation of indigenous tanning materials, and the application of modern tanning techniques, India could be a competitive factor as a leather producer.

Synthetic Leather Oils and Fats. By B. M. Das. *Tanner*, **8**, No. 8, 27, No. 9, 10 (1954). Marine oils are most suitable for leather, the most important being cod oil. During World War II Germany experienced a shortage of marine oils so produced the Dermanols, synthetic oils from the basic synthetic material, Kogasin. This product is obtained from the manufacture of benzene by the Fischer-Troppsch process wherein carbon monoxide is converted into paraffins. Kogasin is the fraction containing C 10 to C 15, with a boiling range of 240 to 320°C. This material is then chlorinated. Where once India had a flourishing marine oil industry, based largely on sardines, this business has dwindled greatly, due to the absence of sardines in the coastal waters. In consequence of this India finds herself in the same position as Germany did. Since India has no facilities for the manufacture of Kogasin, research has been instituted to produce substitute leather oils from Diesel oil.

Studies on Tanning Properties of Chrome Liquor Prepared with Organic Reducing Agents. I. Reduction Efficiency of Some Organic Substances. By Y. Sakimoto and T. Osugi. *Memoirs Fac. Agr., Hokkaido Univ.*, **1**, 361 (1953). The authors investigated the concentration of reactants, reaction time, and calculated basicity on the reduction of $K_2Cr_2O_7$ with methyl alcohol, glycerin and glucose in the production of one bath chrome liquor. The requisite amount of each reducing agent was determined for complete reduction. It was found that the theoretical amount of the reducing agents did not effect complete reduction at a calculated 33.3 per cent basicity. In all cases the higher the $K_2Cr_2O_7$ - H_2SO_4 mixture. The greater the degree of reduction was effected, becoming constant at 3.28 *N* H_2SO_4. The basicity increased proportionally with the rate of reduction. The effect of time upon the rate of reduction was greater at lower concentration. At 3.28 *N* H_2SO_4 methyl alcohol reduction showed no increase after an hour. Glucose was decomposed rapidly during the first reaction period of 17 to 75 minutes. After this reduction proceeded more slowly. Glycerine reduction proceeded smoothly with time. The effect of calculated basicity upon the rate of reduction was readily apparent at lower concentrations, showing up to the greatest extent with methyl alcohol. The efficiency of reducing agents was in descending order: glucose, glycerine, methyl alcohol. At low concentration glucose was not good, however. The quantities of agents for complete reduction were the following percents of the theoretical: glucose 140, glycerine 170, methyl alcohol 260.

Studies on Tanning Properties of Chrome Liquor Prepared with Organic Reducing Agents. II. The Effect of the Amount of Reducing Agent and Aging on the Chemical Characteristics of the Chrome Liquor. By Y. Sakimoto and T. Osugi. *Memoirs Fac. Agr., Hokkaido Univ.*, **1**, 548 (1953). The influence of the amount of reducing agents and aging of chrome liquor upon the chemical characteristics of the liquor were examined. These characteristics included basicity, precipitation figure, and degree of olation of the chrome liquors which were prepared by the reduction of dichromate with methyl alcohol, glycerine and glucose. Variation of the characteristics were then compared with the amount of organic acid produced in the liquor and the amount penetrating the

chrome complex. The results obtained were summarized as follows: basicity as measured by alkaline titration was always lower than the calculated value. The basicity of each liquor was at a mximum when the requisite amount of reducing agent was present for complete reduction of the chrome. Increasing the amount of reducing agent beyond this point had a tendency to lower the basicity. This characteristic was most prominent with glucose. When methyl alcohol was used in amounts over 260 percent of the theoretical for complete reduction, the basicity of the liquor remained fairly constant. In each case the precipitation figure was at a minimum when the requisite amount of reducing agent was present. Increasing the reducing agent beyond this point raised the precipitation figure. Glucose and glycerine produced the same precipitation figure. The amount of organic acid produced in the chrome liquors increased with increasing amounts of reducing agents and there was a proportional relationship between the variation of basicity and precipitation figure. Increasing the amount of reducing agents resulted in the formation of nonvolatile acid. The volatile acid produced was less except in the case of methyl alcohol where the nonvolatile acid remained constant and the volatile acid increased. The amount of acid penetrating the chrome complex increased with aging of the liquor, in all cases except where methyl alcohol was the reducing agent. Here the reverse was true. In all cases olation was not pronounced, and there was no apparent difference in liquors produced by the three reducing agents.

Studies on Tanning Properties of Chrome Liquor Prepared with Organic Reducing Agents. III. Masking Effect of Various Organic Salts. By Y. Sakimoto and T. Osugi. *Memoirs Fac. Agr., Hokkaido Univ.*, **2**, 195 (1954). Potassium Bichromate was reduced with sulfur dioxide after which different amounts of sodium salts of various organic acids were added to the chrome liquors, and these subsequently examined for the purpose of determining the amount of masking agent penetrating the chrome complex. The effects of the addition of the salts on pH values and precipitation figures were also determined. The authors conclude that the amount of acid radical penetrating the chrome complex increased rapidly for forty-eight hours, but after this the penetration proceeded very slowly. Tartrate and citrate reached a constant after forty-eight hours. Citrate and tartrate radicals penetrated to a lesser extent than the oxalate. The pH value of the liquors increased proportionally to the amount of organic salts added. The precipitation figure increased with the increasing amounts of added salts, except in the case of formate. In the case of oxalate the precipitation figure was lowered.

Curing Trials with Sudan Sheep and Goat Skins. By J. R. Furlong and E. Knew. *Colonial Plant and Animal Products*, **4**, 29 (1954). The purpose of the curing trials was two-fold: (1) to compare the effect of using Sudan salt and imported salt in the preparation of dry salted sheep skins, by two methods, (a) native and (b) special. (2) To determine whether exposure of sheep and goat skins to the sun for the purpose of drying during the hot season is injurious. The native curing method was as follows: skins were removed from the carcass in "cased" form and piled in a clean place, without washing. They were defatted, salted on the flesh side after turning the flesh outward. Flesh was then turned inside, each skin rolled in a bundle, and the bundles piled in a heap for 7 days. The skins were then opened down the belly and shanks and hung over a rope in a shed to dry. Time for drying was 24 to 48 hours. In the special cure method the same procedure was followed up to defatting. After this the skins were opened as before, salted, piled flesh up on a lattice rack, and then covered with wet gunny. Skins for pickling were taken after salting to a tannery for conventional pickling. In the sheep and goat skin drying trials, one batch of sheep skins was defatted and, without washing, was dried on frames in the full sun. Another batch, treated in the same manner, was dried over ropes in the shade in a

shed. One batch of goat skins was dried similarly to the first batch of sheep skins. Analysis of results of the alum tanned skins led to the following conclusions: Sun drying in the full sun in the hot season is highly injurious to both sheep and goat skins. Pickling, as carried out in the test, is satisfactory. It is apparent therefore that damage occurs during the drying period. No difference was noted in leathers from skins dry salted by the special and native methods, hence the method of salting does not appear to be a factor. Washing of skins before salting may be a contributing cause of poor cure, but this will have to await further examination. For the present the recommended method of cure is to straight dry over ropes or frames in sheds in the hot season, and in direct sun over ropes or frames in the cold season. While there is some indication that Sudan Salt is not as good as imported salt, the evidence is inconclusive.

An Investigation into the Protection of Dried Hides and Skins. By R. L. Sykes. *Colonial Plant and Animal Products*, **4**, 97 (1954). Hides and skins produced in East Africa were treated for protection against insect, mold and bacterial damage. Goat skin pieces were dipped in the antiseptic solution, then held at temperatures and time periods as noted. Samples treated against insect damage were stored at 20°C. for 18 weeks at 65 per cent R. H. in the dark. Treatment against mold damage consisted of dipping pairs of skin samples in antiseptic solutions, one pair being subsequently inoculated with a suspension of mold spores, and both pairs stored for 30 days at room temperature of 20-23°C., and R.H. of 85-90 per cent. To test against bacterial damage discs of raw skin were paired with similar disks in nutrient broth containing an amount of antiseptic equal to that contained in the dip, and both pairs incubated for 48 hours at 37°C. Antiseptics used against insect, mold and bacterial damage, were zinc chloride, sodium silicofluoride, Chroricide B, Skirlan NA, Santobrite, p-nitrophenol, Dieldrex 15, γ-benzene hexachloride, sodium arsenite and Vantoe A. Sodium arsenite and γ-benzene hexachloride were the most effective against insect damage. Pentachlorphenate and p-nitrophenol appeared to offer the greatest protection against mold, and sodium silicofluoride, Santobrite and sodium arsentie were the most effective against bacterial putrefaction.

Some Notes on Histological Technique. By B. M. Das and S. K. Mitra. *Tanner*, **8**, No. 10, 18 (1954). Sole leather and other hard leather are saturated with paraffin and then imbedded in paraffin before slicing with the microtome. Samples of soft and pliable leathers are placed in the embedding block without previous paraffining. Heavy leathers are best cut on the Heavy Sledge Microtome, and soft leathers on the Minot Rotary Microtome. Leather sections are freed from paraffin by immersing them for a few minutes in xylol. Vegetable leathers are mounted in Canada balsam and chrome leathers in Euparal, a mixture of camsal sandarac, eucalyptol and paraldehyde. Sections of brittle and delicate specimens are fixed to the slide with Mayer's albumen fixative before clearing in xylol. Samples of raw hides and skins are fixed in formol saline before cutting. Pelts from various stages in the tanning process are sectioned directly on the freezing microtome. Gum mixture (consisting of 5 gms. gum arabic, 1 gm. saccharose, 1 gm. boric acid and 100 cc. distilled water) is used to surround the specimen. For the examination of fiber structure sections may be mounted in glycerine jelly without staining. Directions are given for preparing such stains as Weigert's elastin and Delafield's haematoxylin.

Edible Gelatin from Tannery Byproducts. By Y. Nayudamma. *Tanner*, **8**, No 10, 23 (1954). Hide trimmings are washed, limed for 4 weeks or more, unhaired, washed again and delimed with hydrochloric acid so that the final pH of the stock is about 4.5. The hide pieces are placed in water at 70°C., and when this shows a gelatin concentration of 1.5 to 3 percent, it is run off. A second digestion occurs at 80°C. In all 5 extractions are made with the temperature of the water gradually increasing to 100°. Water is evaporated from the first extract, using single or multiple effect evaporators. At a concentration of

12 percent gelatin, the solution is bleached, pH adjusted to 5.5, chilled, cut into strips or cakes, and dried. Edible gelatin must be manufactured under sanitary conditions and strict chemical control. Since quality gelatin depends on quality raw stock, it is to the mutual interest of tanner and gelatin manufacturer to work together to secure the proper raw stock.

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Sl. No. (1)	Name of sample and description. (2)	Moisture. (3) %	Insolubles. (4) %	Tannins. (5) %	Non-tannins. (6) %	Colour (7) Yellow	Red	pH (8)	Remarks. (9)
1.	Rhizophora Mucronota collected from the backwaters of Richavaram in South Arcot district.	9.20	60.50	16.60	13.70	17.0	4.0	4.4	As it contains about 17% tannins, it compares well with 'Avaram bark' with the added advantage of a considerably high percentage of yellow colouring matter. Thus it appears quite suitable for South India Tanning.
2.	Aegiceras Corniculatum collected from the backwaters of Richavaram.	9.50	62.10	14.00	14.40	8.4	2.4	4.4	This contains a comparatively high percentage of tannin and compares fairly well with Avaram. The higher proportion of yellow colouring matter appears to be quite suitable for South India Tanning.
3.	Sonneratia Apetala collected from the backwaters of Richavaram.	9.60	59.50	16.6	14.3	10.0	2.0	4.4	As it contains about 17% tannins, it compares well with 'Avaram bark' with the added advantage of a considerable high proportion of yellow colouring matter. Thus it apears quite suitable for South India Tanning.
4.	Dolichandrone Spathacea (Tann. Vilpade) collected from the backwaters of Nileshwar.	10.60	73.30	3.30	12.8	16.1	11.3	4.8	Since it contains only a very low percentage of tannins it may not be much use for the tanning trade.
5.	Sundri (Heritiera Fomes) supplied by Government of India.	8.00	82.71	4.92	4.37	10.5	7.5	5.2	do It contains fairly good percentage of tannin.
6.	Hari Taki supplied by Government of India.	10.24	60.84	22.48	6.48	7.1	4.2	3.6	It may be of use in heavy leather tanning-especially sole leathers.

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7.	Sonari (Caesalpincacea) (Cassia Fistula Linn) samples collected from Vizagapatam.	7.94	75.20	11.64	5.22	10.0	16.5	3.6	It contains about 12% of tannin. Since the percentage of red colouring matter is fairly high, it can be used for heavy leather tanning, especially sole leathers.
8.	Khari-wood supplied by Government of India.	9.20	75.80	9.60	6.00	4.9	2.8	5.2	As the percentage of tannin in this bark is low it may not be of much use for the tanning trade.
9.	Keora bark (Sonneratia apetala) supplied by Govt. of India.	9.50	82.50	3.72	4.30	10.0	4.0	5.0	Since it contains only a very low percentage of tannin, it may not be of much use for the tanning trade.
10.	Small Goran (Ceriops roxburghiana) supplied by Govt. of India.	10.10	63.90	16.80	9.20	15.0	16.0	5.4	As it contains fairly high percentage of tannin, and a high proportion of red colouring matter, it may be profitably used for sole leather tannage.
11.	Pasur Bark supplied by Govt. of India.	9.60	69.30	14.0	7.1	16.0	9.0	5.0	This contains a comparatively high percentage of tannin and compares fairly well with Avaram. The higher proportion of yellow colouring matter appears to be quite suitable for South India Tannage.
12.	Garjan bark supplied by Govt. of India.	9.80	58.40	24.4	1.40	16.0	17.0	5.2	This may be of great use for sole leather tannage.
13.	Matgoran bark supplied by Govt. of India.	9.70	62.40	19.90	8.00	16.0	8.0	5.6	It appears quite suitable for South India Tannage.

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14.	Dhundal (Xylocarpus Gramatun) supplied by Govt. of India.	10.20	70.20	13.20	6.40	17.0	8.0	5.8	It appears quite suitable for South India Tannage.
15.	Karada Bark supplied by Govt. of Orissa.	10.80	59.30	19.60	10.30	3.0	3.4	5.5	It can be used for sole leather tannage.
16.	Avaram (Cassia auriculata) from Kanigiri range Nellore.	8.00	63.85	16.73	11.42	4.0	1.0	4.4	It is being extensively used in the South Indian tanning trade.
17.	Cassia auriculata from Kavali range Nellore (10 months old and four feet height)	8.00	76.53	10.67	4.8	4.2	1.2	4.4	do
18.	-do- plants of 8 months old and three feet high.	8.10	59.63	22.27	10.09	3.0	1.0	4.4	do
19.	-do- plants of 6 months old and two feet high.	7.80	60.93	21.47	10.08	3.5	1.0	4.4	do
20.	Avaram bark (Cassia Auriculata). from Udayagiri range (plants over three years).	6.20	60.44	21.18	12.18	3.5	1.0	4.6	do

S. No. (1)	Name of sample and description. (2)	Moisture. (3) %	Insolubles. (4) %	Tannins. (5) %	Non-tannins. (6) %	Colour (7) Yellow	Colour (7) Red	pH (8)	Remarks. (9)
21.	Avaram bark (Cassia Auriculata) from Udayagiri range (plants over two years of age).	7.10	59.90	17.34	12.66	4.0	1.0	4.6	It is being extensively used in South Indian Tanning Trade.
22.	do. (plants over one year of age.)	8.20	60.05	19.27	12.48	4.2	1.2	4.6	do
23.	Avaram bark (Cassia Auriculata) from Udayagiri range (plants within one year of age).	8.80	60.08	20.42	11.70	3.0	3.2	4.6	do
24.	Wattle bark (Acacia Mollisima) from Nilgeris division (from 1942-43 plantations.)	9.50	44.21	34.86	11.43	3.8	1.5	4.4	It is being extensively used in South Indian Tanning Trade as well as in heavy leather tannage.
25.	do. (from 43-44 plantations).	11.0	44.93	33.7	10.37	4.0	1.5	4.4	do
26.	do. (from 44-45 plantations).	8.50	46.61	32.32	12.57	4.0	1.5	4.4	do
27.	do. (from 45-46 plantations).	9.70	43.65	35.10	11.56	4.0	1.5	4.4	do
28.	-do- (from 46-47 plantations).	9.50	39.45	38.75	12.37	4.8	2.0	4.6	do

S. No. (1)	Name of sample and description. (2)	Moisture. (3) %	Insolubles. (4) %	Tannins. (5) %	Non-tannins. (6) %	Colour (7) Yellow	Colour (7) Red	pH (8)	Remarks. (9)
29.	Wattle bark (Acacia Mollisima) from Nilgiris division (from 47-48 plantations).	8.36	44.13	36.1	9.41	4.8	2.0	4.6	It is being extensively used is South Indian Tanning Trade as well as in heavy leather tannage.
30.	-do- (from 48-49 plantations).	9.10	40.25	37.89	12.76	3.5	1.7	4.6	do
31.	Hopea Parviflora from South Canara division.	7.6	63.5	20.17	8.73	7.5	2.5	4.4	This bark is found to be very useful in heavy leather tannage.
32.	Babool (Acacia Arabica) from Guntur division.	10.0	61.46	20.6	7.94	15.0	5.0	4.0	This bark is being used in heavy leather tannages.
33.	Dhawa Sumach leaves (Angoissus Latifolia) from Mamandur in Chittoor dist. (Middle aged leaves).	10.0	52.00	30.0	8.0	5.0	20.0	4.8	It contains a very high percentage of tannin and is also found to be very useful for South Indian tanning.
34.	-do- (tender leaves from Cumbum in Madurai district).	10.0	46.30	26.60	17.20	10.0	12.5	4.8	do
35.	-do- (Matured leaves from Cumbum Madurai district).	10.0	61.63	14.20	14.27	10.0	5.0	4.6	do

S. No. (1)	Name of sample and description. (2)	Moisture. (3) %	Insolubles. (4) %	Tannins. (5) %	Non-tannins. (6) %	Colour (7) Yellow	Red	pH (8)	Remarks. (9)
36.	Karada bark from Nellore division.	10.8	59.3	19.6	10.3	3.0	3.4	5.5	It may be of much use in the production of leathers of inferior quality.
37.	Terminalia Arjuna bark supplied by the Forest Department.	11.2	60.0	19.43	9.37	10.0	5.5	5.0	It is found to be useful in heavy leather tannage.
38.	Indian Red wood bark from Onepenta range).	8.0	65.0	15.0	12.0	14.0	6.0	5.3	It is found to be useful in the production of sole leather.
39.	Malabar Teak bark (Terminalia Grandis) from Mannantoddy in Malabar district.	6.46	74.49	2.91	16.14	3.8	1.5	4.8	Since it contains only a very low percentage of tannin, it may not be of much use for the tanning trade.

It is seen from above table, that there is a good number of indigenous tanning materials containing a fairly high percentage of tannin. A detailed and complete study of some of these materials is bound to yield substantial results.

The analysis of the avaram and wattle barks were done with a view of determining the optimum age of the plants at which they yield the maximum of tannin.

Prospects in Leather Technology. By B. M. Das. *Tanner*, **9**, No. 2. 22 (1954). The technology of leather manufacture covers an extremely broad field and requires specialized knowledge in many fields of scientific endeavor. India is doing much to train men in the science of leather manufacture, and is placing them in plant and laboratory where they can develop the industry along modern lines.

A Study of the Use of Indigenous Oils, Including Fish Oils, in the Leather Industry. By P. S. Chowdary, K. A. Joseph and K. Padmanabham. *Tanner*, **9**, No. 4, 13 (1954). Because it is more economical to use native oils in place of imported cod oil, the authors have investigated two native oils which have proved satisfactory in their application to leather. The one is pungam oil from the seeds of the tree Pongainia glabra. It has a bitter taste and unpleasant odor. Neem or Margosal oil is from the seeds of Melia azadirachta. It has a strong garlic odor. Properties of the oils are as follows:-

	Pungam Oil	Neem Oil	Fish Oil
Sp. Gr.	0.92- 0.94	0.915-0.918	-0.895
Acid value	6.36-11.10	5.0 -36.0	39.2
Saponification value	176- 189	180.0- 198	170.4
Iodine value	83 - 94	63.0-71.9	115.9
Unsaponifiables	2.3- 9.0	0.70-1.47	2.66
Compositions are:			
Palmitic acid	6.06	13.6	
Stearic acid	2.20	19.1	
Oleic acid	61.30	49.0	
Linoleic acid	9.72	15.8	

The fish oil shown above was obtained from the livers and blubbers of unnamed fish. Fish and pugam oils were found to be suitable for stuffing mixtures, but neem oil was unsatisfactory. Neem oil charred during sulfonation, and sulfonation results were not very promising with pungam oil. Sulfonated fish oil was fairly satisfactory. Impurities in the raw oil, such as foots, have been causing more or less trouble, hence a purfied oil would find more ready use.

Mold Growth on Some of the Indian Vegetable Tanning Materials. By E. C. George. *Tanner*, **8**, No. 9, 20 (1954). After reviewing the literature on the type of molds found in vegetable tanning materials, the author states that an investigation has been instituted of the mold growth in the principal Indian tannins. These include myrobalams, divi divi. iron wood. babool, avaram, karada and konnam. The foregoing materials were first crushed and then soaked in water, the ratio being 10 grams of material to 50 cc. of water. Myrobalams and divi divi showed mold growth within 24 hours, babool, avaram and konnam within three days. Ironwood and malabar showed no mold growth even after a long while. Mold growth was vigorous in all liquors except ironwood and malabar. In babool, however, the growth was rather slow and appeared as a whitish mass. Karada mold was dark brown, konnam dark green, and divi divi yellowish. The foregoing observation led to the conclusion that the molds were different with respect to structure, origin and development. The molds on myrobalams were identified as Aspergillus Niger and Mucor racemosus, that on divi divi as A.flavipes, that on karada as Aspergillus elavatus, that on konnam as Aspergillus fumigatus, on avaram as Aspergillus Niger, and that on babool as some form of Aspergillus. In some cases certain species of Penicillium were also seen.

A Study of Dhawa Sumac Leaves *(Anogeissus Latifolia)* as a Suitable Tanning Material. By P. S. Chowdary, K. A. Joseph and K. Padmanabhan. *Tanner*, **8**, No. 9, 23 (1954). Anogeissus latifolia is a moderate to large sized deciduous tree bearing local names of vellaynaga, chiriman, dindal, dinduga, dhaura, dhau, dhawa and bakli. It is found from the outer Himalayan slopes to Central and South India. Its wood is relatively hard and dense. It yields dhawa or gum ghati of commerce, while from the leaves a black dye is obtained. An extract, containing 43.8 per cent tannin, has been produced from the bark. The leaves, however, are the principal source of tannin, and by analysis showed the following:

Origin and Nature of Sample	Tannin	Soluble Nontans	Insolubles	Moisture
Tender leaves Cumbum in Madure Dist.	32.87	14.21	42.92	10.0
Middle Aged Leaves from Mamandur in Chittoor Dist.	24.27	14.4	51.33	10.0
Matured Leaves from Cumbum in Madura Dist.	15.21	13.2	61.59	10.0

Tender leaves are about as rich in tannin as wattle, divi divi, and myrobalams. Its pH is about the same as wattle, namely 4.4, but it imparts a yellowish color, rather than a pink, to the leather. The leaves are readily extractable, about 50 per cent of the tannin being removed in the first 24 hours. Practical tanning tests with dhawa sumac liquors produced a somewhat empty and flat leather whose color did not meet expectations. The degree of tannage was good, however, being about about 74.

The Application Of Coated Abrasives In Leather Tanning. By J. F. McCormack. *Leather and Shoes*, **129**, No. 1, 17 (1955). Sandpaper, or other coated abrasive, is actually made of thousands of little cutting tools. The original natural minerals used in coated abrasives were flint, emery and garnet and are still in use today. However aluminum oxide grain has today surpassed all of the above, and employing the electro-coating method has improved the quality of coatings tremendously. The sandpaper industry is the largest user of animal hide glue in the world today. There have been great changes in the development of suitable equipment for buffing and snuffing leather in the past twenty years. From the use of machines which sanded a path only eight inches wides, equipment is now available that takes a whole side of leather in one pass. The author predicts improvements in the future design of sanding machines such as the use of soft rubber covered cylinders. In leather buffing there are many varing factors which make the job slightly different from one plant to another, even though primarily the same type of chemicals, oils and other ingredients are used. Examples are, temperatures in drums, penetration of oils or lack of penetration, the washing of surfaces after their baths in chemicals, dyes and oils. Scratches can be caused by sandpaper but favorable surface conditions of the leather would aid considerably in offsetting this possibility. The types of oils and pastes used have quite a bearing on the life and cutting qualities of a sandpaper. The author deals with various types of leathers and the grit and kind of sandpaper best suited to them. R.B.K.

The Influence Of Depilation On Grain Of Leather. By R. Davis. *Shoe and Lea. Reporter*, **277**, No. 9, 11 (1955). By proper depilation, keratin and all extraneous matter is removed, so that collagen fibers alone remained to be tanned. Up to about 15 years ago depliation required from 5 to 7 days in limes sharpened with dimethyl amine, arsenic or sodium sulfide. Now it is not unusual to dissolve the hair in a two per cent sodium sulfide solution within two hours. In such cases the hides have to be removed before they are damaged by the sulfide, washed and subsequently limed. Sodium sulfide is used as an additive to lime liquors to hasten their action on the hair and epidermis. It is also an ingredient of lime paste or paint where this form of unhairing is in use. Sodium sulfhydrate is neutral in acqueous solution and when added to lime liquors it forms but half the caustic soda that sodium sulfide does. Consequently it does not raise the pH of the limes. It makes possible a more complete separation of the keratin from collagen without damage to the latter. Undue swelling is avoided, and a fine, smooth grain is produced, resembling the grain of hides limed by the long, mellow liming process. The time is reduced to approximately two days and it is possible to save the hair when using the sulfhydrate. With respect to goatskins, the amines are favored because of their ability to split the fibers and to produce an exceptionally fine grain. Other depilatories and modifications of the aforementioned processes are referred to briefly. R.B.K.

Do Changes In Leather Manufacture Affect Finishing Procedures. By J. Quinn. *Shoe and Leather Reporter*, **277**, No. 8, 19 (1955). It is brought out that changes take place in tanneries that are beyond any one's control, even in normal processing. These changes alone give the finishing department plenty of trouble. If there are any slight changes actually made, such as lighter or heavier buffing or some change in the wet work that tend to vary the absorbency of the leather, these facts should be brought to the attention of the finishing department. Any deviation from normal procedure may not only affect the break of the leather and the surface characteristics, but might well affect the shade enough so that whole loads of leather would be off for no apparent reason. It would definitely be good business to keep the finisher well informed as to any changes made or contemplated, no matter how slight. R.B.K.

What Are Purposes and Qualities Of Top Finishes Used Today? By W. Cronin, Jr. *Shoe and Leather Reporter*, **277**, No. 8 18 (1955). With exceptions, top finishes must be watertight without being waterproof, so that the leather can be dressed later in the shoe factory. Due to the improvement of raw maerials such as the better refining of waxes, gums, shellacs, et cetera. and the introduction of synthetic resins, synthetic waxes, shellacs and latices, the finish manufacturers are able to formulate newer and better top finishes. Regardless of the standarization of application in many cases, top finishes must be fitted to the types of leather being made. Also top finishes will react differently when subjected to different types of ironing or plating. Various kinds of leathers are grouped because of approximately the same requirements. Baggage, luggage and garment leathers constitute one group, upper leather represents another and shoe linings a third group. Necessary qualities of top finishes for each leather are cited. R.B.K.

What Is A Lacquer? By P. Shoer. *Shoe and Leather Reporter*, **277**, No. 8, 14 (1955). The author discusses the makeup and application of conventional lacquers based on nitrocellulose. The use of dyes in lacquers and pigments are mentioned. The hazards of using the lacquers, from a standpoint of their being highly inflammable, are brought out and certain safety precautions are stressed. Lacquer emulsions are next considered. There are two types of lacquer emulsions, which are the water thinned and the solvent thinned types. In general, if the lacquer is added to the water, a water thinned emulsion is formed. If

this order is reversed a solvent thinned emulsion results. The biggest advantage of lacquer emulsions is their safety in the tannery and the safer of the two is the water thinned emulsion. One of the good characteristics of a water thinned lacquer emulsion is the tendency to stay on the surface of the leather. It is used for clear films that are to remain on the surface. For better penetration and a little higher gloss the solvent thinned emulsion should first be tried. It can very easily be pigmented and dyes can be added without difficulty, making it the best emulsion for aniline work. Storage of the two emulsions present no unusual problem aside from the fact that they should be protected from freezing. It is better to have a lacquer emulsion of relatively high flash point and in no case should it be less than 100 degrees F. R.B.K.

Study On The Tannin Distribution In Vegetable Tanned Leather. By M. Banerjee and S. K. Sarker. *Tanner*, **9**, No. 5, 19 (1954). Three samples of vegetable tanned cow hide were taken for microscopical study and chemical analysis. Microscopical studies distinctly showed three layers, namely, grain, middle and flesh. Photo-micrographs are included. Grain and flesh layers were more deeply colored than the middle layer. Thickness of the different layers and the results of the chemical analysis are given in tabular form. Analysis showed that the per cent of water soluble matter is always lower in the middle layer and combined tannin highest. As the tan liquor penetrates the hide, the grain and flesh layers filter out a large portion of the coloring mater, with a partial removal of nontans. The liquor finally reaching the middle layer is rich in tannin and produces a more fibrous and compact layer than either the grain or flesh. It is seen from this investigation, that the distribution of tannin is not uniform throughout the layers but is highest in the middle layer. R.B.K.

Vegetable Tanning Materials In Pakistan. Goran Bark. By S. M. Rahim. *Tanner*, **9**, No. 7, 23, (1954); No. 8, 13 (1955). Goran bark (*veripos roxburghiana*) is a species of mangrove bark. The various species of mangrove bark are similar except in tannin content which will vary from negligible to as high as 40 per cent. A good quantity of goran bark is used by the heavy leather industry in India, particularly for the tanning of sole leather. The objection to goran is that it gives a dark colored, flat leather having a brittle grain, when used alone. Qualities of goran affecting the tannage are, high salt content, color and astringency. Marketability of goran will depend on availability, accessibility, cost of collection, quality and demand. A blend of 1 part goran, 1 part wattle and 1 part myrabalam, on tannin basis, will yield a sole leather of good color. Goran tannin requirements for use in sole leather being manufactured in Pakistan would take the production of a 5 ton a day extract plant. The tannin content of leaves from the goran tree is between 10.0 and 12.9 per cent depending on the age of the leaves. The bark may contain 37 per cent air dry tannin and the fruit around 6 per cent, while the tannin content of the wood is negligible. References are given citing comparison of mangrove with quebracho, wattle, chestnut and myrabalam, as to penetration, astringency, combining capacity, loss of tannin in tan liquors, color of extracts, brightness and pH. From the data given the author concludes that mangrove bark is an exceptionally stable tannin and causes almost no loss of tannin in tan liquors. The proportion of firmly combined tannin is very high due to its large molecular structure and therefore the yield of leather and firmness are entirely satisfactory. Three drawbacks of mangrove tannin are given, astringency, objectionable color and high salt content. To decrease astringency the tannin may be sulfited, salts of weak acids may be added to mellow it or it may be blended with other mellow tanning materials in the right proportions. Any of the above treatments would also improve the color. While, in actual tanning practice, the high salt content has little effect in cold liquors, in hot pit liquors, adjustments in acid content and temperature are necessary, otherwise serious loss of weight and natural firmness result. In extracting mangrove bark too high

temperatures are to be avoided, the most practical temperature being 50 to 60C°. The author gives recommendations as to measures that should be taken by the government to expedite production of goran extract. R.B.K.

Advantages of Using Elastothiomers for Processing Industrial Leathers. By T. A. Dickinson. *Lea. and Shoes.* **127,** No 14, 15 (1954). Elastothiomers is a term used to designate a group of double decomposition products of various dihalides and alkali polysulfides. The best known and most widely used elastomers of the organic polysulfide polymers are the Thiokols. Their most desirable properties are excellent solvent resistance, unexcelled gas impermeability, good aging characteristics, resistance to ozone, ability to remain flexible at extremely low temperatures, and compatability with other elastomers which lack such qualities. Leather, impregnated with Thiokol liquid polymers, makes excellent shaft seals, gaskets and packings. When such treated leather is used as components of dry cleaning equipment, they are unaffected by such solvents as CCl_4 and trichlorethylene. When used as packings in pneumatic and hydraulic equipment, the impregnated leathers can prevent leakage at operating pressures exceeding 2000 pounds per square inch. Leathers are usually impregnated with an ethylene dichloride dispersion of the elastothiomers. R.B.K.

New Developments in Upholstry Leather. By F. O'Flaherty. *Shoe and Lea. Reporter,* **276,** No. 8, 25 (1954). Within a generation there has been more technological advancement in the manufacture of upholstry leather than in all the decades which preceeded this period. Modern electronic equipment is used for the control of temperature, volume and chemical reactions. Quality controls are on a scientific basis and testing is done on a sound statistical basis. The internal surfaces of leather, equal to 50,000 times the outer surface, are being intensively studied at the University of Cincinnati and the Bureau of Standards. It is these internal surfaces which contribute to the comfort which leather provides. Research on oils has resulted in new and improved lubricating methods whereby each internal surface is lubricated. By means of Hunter Color Difference Meter, the upholstry tanner is able to match any color to provide special shades of various colors. New finishes have been developed which enhance the leather, but still permit the feel and look of leather. Since leather is almost always used under dynamic circumstances in service, dynamic test methods have been developed. These include tensile strength, static and dynamic stitch tear, scuff, abrasion and flexing tests. The data illustrating these tests show leather to be superior to any other materials. Research and technical developments are continuing under the direction of the Technical Committee of the leather industry.
R.B.K.

What Qualities Make a Good Finish. By M. Castleman. *Shoe and Leather Reporter,* **277,** No. 8, 13 (1955). The two aims in finishing leather are to give it beauty or sales appeal and a protective coating so it will wear better. The first quality demanded of a good leather finish is that it produce a good break on leather. Thorough dispersion of pigments gives maximum coverage with the least pigmentation. The second quality is leveling, which may be influenced by factors such as grain being snuffed unevenly, uneven distribution of oil or tanning materials, paste not being evenly removed, or the use of hard water. The third quality desired is uniformity with the buyer expecting the finish to have the same shade, same tinting strength, the same brightness, the same pH and the same viscosity. The author gives some typical finish color problems that have caused troubles in tanneries and remedies to correct them. A finisher should know what is required of the leather and how to make simple test to insure that his leather is up to requirements.
R.B.K.

Resins In Leather Finishes. By R. Shaw. *Shoe and Leather Reporter,* **277,** No. 8, 16 (1955). Water finishes represent the bulk of the finishes used in most leathers. A wide variety of synthetic resins are today available but not all are suitable as components of a leather finish. For resin to be usable it is necessary to have a soft material with a great deal of stretch in order for the finish to stand up to repeated flexing without cracking. At the present time only the acrylics, methacrylics and various synthetic rubbers meet the necessary conditions, at least for use in water finishes. To be used in water finishes it is necessary to have these synthetic resins in a water dispersion in order to mix with the other components of such finishes. This is accomplished by carrying out the manufacture of the resins in a water system, and is known as emulsion polymerization. By proper choice of emulsifying agents and proper conditions the resin is obtained, dispersed in water, in a very fine form. Methyl acrylate gives the hardest straight acrylic resin. Ethyl acrylate on polymerization gives a much softer resin with much more stretch, but also with increased tack. This trend continues with the higher alcohols such as propyl, butyl, et cetera. In the methacrylics for the same alcohol the resins formed are considerably harder, in fact, it is not until the butyl ester is reached that a usable product from a standpoint of softness and stretch is obtained. Synthetic rubbers, produced by the polymerization of butadiene, are too soft for leather firmness. It is customary to harden and toughen them by copolymerizing them with monomers such as styrene and acrylonitrile. The acrylic and methacrylic resins when polymerized give completely saturated materials and are therefore very stable and permanent, thereby imparting the property of lasting flexibility. Butadiene polymers on the other hand are still unsaturated materials which can undergo changes, particularly oxidation, with consequent loss of flexibility. The general tendency is for the synthetic rubbers to fill somewhat more, the acrylics to penetrate better. In using synthetic resin emulsions in a water finish for side leather they are added to the other materials present, such as proteins, waxes, pigment dispersion, et cetera and the finish applied in the regular way. While resins do not solve all the problems encountered in leather finishing they help, by improved surface filling, flexibility, adhesion of the finish, wet rub resistance and making possible application of a subsequent lacquer coat with good adhesion. R.B.K.

Aquatic Life Water Quality Criteria. By the Aquatic Life Advisory Committee of the Ohio River Valley Water Sanitation Commission. *Sew. and Ind. Wastes,* **27,** 321 (1955). In this first progress report the Committee has outlined the scope and policy of its undertaking and discussed the development of water quality criteria in the light of available literature. The general approach to the problem is stated as follows: In the setting of water quality criteria the committee believes that attention should be given primarily to the condition of the stream after it has received the pollutant rather than to the nature of the individual effluents which empty into it. After suitable stream conditions have been determined, the various effluents can be adjusted to maintain the desired stream quality. The problems and difficulties which will be encountered in this type of approach are not minimized, but any other will fail to achieve the end sought. Since producing an effluent which will not kill fish when acting alone is no guarantee that this material when combined with others already in the stream will not prove harmful, final condition of the stream will be the basis of evaluation. It is realized that much work must be done on each local problem to determine the exact amounts of material which can be placed in a stream of various levels of water flow before final requirements for individual pollutors can be made. To accomplish prompt results, the commmittee believes that minimum requirements should be set at a level where the effluent after it enters the river has no acute toxicity to fish or measurable deletrious effect on aquatic organisms as measured by bioassay. Because the toxicity of most materials varies with the quantity and type of other materials in the waste and with the nature of the receiving water, it is considered to be impractical in most cases

to set standards in terms of parts per million. The committee therefore recommends that water quality criteria be established in terms of bioassay carried on in accordance with standard procedures approved by the committee. In regard to dissolved oxygen requirements the Committee has recommended that until further research indicates that a reconsideration is advisable the minimum permissable oxygen concentration for a well-rounded warm water fish population shall be as follows: The dissolved oxygen content of warm-water fish habitats shall be not less than 5 p.p.m. during at least 16 hr. of any 24-hr. period. It may be less than 5 p.p.m. for a period not to exceed 8 hr. within any 24-hr. period, but at no time shall the oxygen content be less than 3 p.p.m. To sustain a coarse fish population the dissolved oxygen concentration may be less than 5 p.p.m for a peeriod of not more than 8 hr. out of any 24-hr. period, but at no time shall the concentration be below 2 p.p.m. The committee further recommends that dissolved oxygen determinations be made in accordance with the procedures specified in the 10th Edition of "Standard Methods". pH requirements have been considered with the following recommendations: 1. That pH be recognized as a poor criterion for the expression of toxicity of acids and alkalies in general, and that its use be restricted to the control of the addition of highly dissociated inorganic acids and alkalies known to be non-toxic within the pH range of 5 to 9. 2. That at no time shall acid be added in quantities sufficient to lower the pH below 5, nor alkalies sufficient to raise the pH above 9; and that, insofar as possible, pH values be mantained between 6.5 and 8.5 to maintain the productivity of the water for aquatic life. 3. That the addition of ammonia (as NH_3 or NH_4OH), poorly dissociated inorganic acids, and organic bases and acid shall be regulated not in terms of pH, but in terms of their own toxicities as established by bioassay. The Committee has also given consideration to the criteria for judging toxicity of wastes by bioassay and has made the following recommendations for controlling the disposal of toxic wastes: 1. The toxicity of wastes to aquatic life in the receiving water can most effectively and reliably be determined by means of bioassays. 2. The biossay methods for the evaluation of acute toxicity of industrial wastes to fish described and recommended by the Committee on Research, Sub-committee on Toxicity, Section III, Federation of Sewage and Industrial Wastes Associations are endorsed. 3. The final concentration of any waste in the receiving water should be no greater than the 48-hr. TL^m X 0.1 (that is, the 48-hr. TL^m as determined by the bioassay methods recommended multiplied by O.1, the tentative application factor). TL^m is the concentration of the substance or waste in question which kills one-half the animals in a specified period of exposure. Other application factors may be used in specific cases, but only after thorough investigations justifying their use have been made. The Aquatic Life Advisory Committee, in recommending the bioassay method as a practical and applicable method for measuring the toxicity of wastes to aquatic orgnisms in waters receiving such wastes, recognizes that there are certain limitations to the application of the method which definitely affect interpretation of the results. Consequently, the person or persons attempting to apply bioassays to the problem must use considerable judgment in organizing each test, such as the selection of test animals, etc. Considerable care must be used in the drawing of conclusions to recognize limiting factors in each test. Therefore the committee recommends that bioassays be conducted by persons of recognized experience and training in this field. This recommendation is made for the sole purpose of assuring that the results obtained from bioassay test be of the highest quality and greatest reliability. J.F.W.

The Dyeing of Leather with Anthrasol Dyes. By W. Lassmann. *Das Leder*, **5**, (1955). Vat dyes, to which the light-fast indanthrene dyes belong, are water insoluble compounds that are changed to a soluble leuco form by reduction in strongly alkaline medium. The leuco form usually has a different color. After absorption on cotton or artificial silk the insolubility and original color are restored by oxidation. Anthrasol dyes

are water soluble sodium salts of sulfuric acid esters of reduced vat dyes. With these the leather can be dyed in a neutral or weakly acid solution instead of a strongly alkaline solution. They are made by reducing a vat dye in pyridine with iron to the leuco compound, and then esterifying with chlorosulfonic acid and neutralizing to form the sodium salt. Leather is dyed by treating it with the anthrasol dye in neutral or weakly acid solution, after which it is transferred to a second vat for saponification and oxidation. Unfixed dye is scrubbed out at 60°C. Saponification may be by one of the three following methods: (1) *Sodium nitrite process.* The leather is treated with anthrasol dye solution containing sodium nitrite, then with sulfuric acid. The acid saponifies the ester to the free leuco compound and also liberates nitrous acid, which readily changes to oxidizing nitric acid. The leuco dyes are sensitive to light, so the saponification and oxidation must be done rapidly. The leuco dyes are all di-esters, except anthrasol blue IBC which is a tetra-ester. On saponification the color changes from yellow to red, to blue as the tetra-ester is changed first to di-ester, then to leuco compound. The oxidized compound is also blue. This dye contains 2 imino groups. Overoxidation may result in the removal of the 2 imino hydrogen atoms and production of a yellowish color, but overoxidation can be prevented by addition of urea. (2) *Potassium dichromate process.* After saponification and oxidation with sulfuric acid and dichromate, the residual dichromate color can be removed by a short treatment of the leather with formic acid and bisulfite solution. (3) *Aluminum chlorate process.* The leather is treated with the dye solution containing tartaric acid and aluminum chlorate, after which it is irradiated with a strong arc lamp. Anthrasol dyes are characterized by fastness not equaled by other dyes. Because they are water insoluble they do not bleed, and have good stability to washing and to sweat. Their pigment-like character results in good covering and uniform appearance, although chrome spots or blemishes are, of course, not concealed. Tests showed, that the oxidation of the dye on the leather did not weaken the leather at all. Examples are given of dyeing various leathers. To dye glove leather, brush the dye solution containing sodium nitrite and urea onto the leather, then either pour 3 percent sulfuric acid at 60°C. over the leather, or paddle the leather for 15 minutes in cold 3 percent acid. Repeat as necessary to give the desired shade, then neutralize with sodium or ammonium bicarbonate. Remove unfixed dye by treating in a vat for 45 minutes with Hostapon TS at 60°C. Fatliquor in another vat. Dye on the flesh side is only on the surface and can be removed easily by shaving the dry leather. I.D.C.

Studies on Suede Dyeing. I. By K. Eitel. *Das Leder*, **5**, 290 (1954). The suede leather user requires; (1) a brilliant shade, (2) uniformity of lots and of skins within lots, (3) complete penetration of dye, (4) good cutting value, and (5) good fastness to rubbing. The effect of chrome content on take-up of dye was investigated in a practical test in which 4-5% of chromium oxide (dry leather basis) was introduced in a pretannage, then this was increased to the following series by a dry tannage with a 50% basic, cationic liquor: 6.3%, 7.7%, 9.9%, 11.7% and 14.3% chromic oxide. The maximum take-up of direct black dye (amount of dye used, 15%) was found with 8% chromium oxide; more than8% oxide in the leather resulted in weak shades and poor bath exhaustion. The best time to achieve brilliance and proper tone is during application of the final finish coat. Brilliance also can be increased by use of the minimum amount of ammonia and maximum practicable temperature in the dye bath. Good cutting value is obtained by use of good raw stock; a short soak with a bactericide and a wetting agent; a short, sharp lime with no salt or calcium chloride; a longer bate than usual; and a high chrome content. A desirable, thick, short nap is obtained by a high temperature during the second tannage and by low tension during tacking. I.D.C.

Commission reports of the VGCT. *Das Leder*, **5**, 297 (1954). The commission for the quantitative analysis of vegetable tanning materials reported (W. Grassmann) that (1) a comparison would be made of the Koch and ALCA extractors after some modification of the latter; (2) revision of the filter method was planned and that (3) a comparative test of 4 prechromed hide powders for the filter method had been made with results shown in the following table (all values have been rounded to 1 decimal):

Hide powder	Lab.*	Moisture	Blank test mg.	Ash %	pH	Nontannin Wattle %	Nontannin Quebracho %	Nontannin Chestnut %
	F	15.5	3.9	1.1	5.3	18.2	8.0	16.6
Darmstadt	R	16.6	5.4	0.9	5.4	16.1	7.0	13.7
Lot 70	D	12.7	8.6	1.0	5.1	16.6	5.6	15.6
	I	13.2	3.4	1.1	4.9	15.8	5.7	13.5
	F	8.3	8.0	1.0	5.7	18.5	8.3	17.2
Freiberg	R	9.4	8.4	0.9	5.6	16.5	7.6	14.1
Lot 144	D	9.7	8.6	1.0	5.2	16.0	6.8	15.5
	I	8.8	5.2	1.0	4.7	16.2	6.3	13.9
	F	11.6	3.7	0.6	5.4	17.8	7.9	17.3
Vienna	R	12.3	2.4	0.5	5.5	15.1	5.9	13.9
	D	12.3	3.6	0.6	5.1	15.5	5.4	15.1
	I	12.0	1.2	0.6	4.8	15.3	5.4	13.5
	F	13.5	3.6	0.6	5.3	17.2	6.6	16.4
French	R	14.2	1.6	0.5	5.5	14.9	5.7	13.0
EFT6	D	14.5	2.7	0.6	5.0	15.4	4.9	14.0
	I	13.8	1.4	0.6	5.0	14.9	5.1	12.6

* F Freiberg laboratory; R Regensburg laboratory; D Darmstadt laboratory; I average results from 4 Italian laboratories.

Progress reports were also made on Leather testing, Fats and Leather dyeing. A comparative test is to be made with several leather abrasion machines. I.D.C.

Trip Reports on the Leather and Shoe Industries in the U.S.A. Some Differences between American and European Leather Technology and Reasons Therefore. By G. Mauthe. **Impressions on a Trip to the American Leather Industry in February, March, and April 1954.** By G. Otto. **Tannery Machines in the U. S. A.** By A. Brill. *Das Leder*, **5**, 265 (1954). Reports at the annual VGCT meeting. I.D.C.

Chrome Salts of Higher Fatty Acids. By A. Küntzel and O. Mischitz. *Das Leder*, **5**, 285 (1954). Previous work on chrome soaps has been on soaps of the lower fatty acids, and was limited to the bad effects of these soaps on the leather properties, such as dyeing, oiling, or spue formation. In the present work, chrome soaps were made of the fatty acids containing up to 18 carbon atoms. The sodium salt of the acid was added to a chromium chloride solution containing 1.2 grams of chromium per litter. The molar ratio of acid to chromium varied from 0.2 to 8. Based on behavior of the soaps, the acids were divided

into 4 groups. *Group 1*: formic, acetic propionic acids. On adding the fatty acid salt to the chrome solution there was first a buffering action and a change in color from blue to bright green. This was followed by a secondary reaction during which, in step 1, the color changed to blue-violet, then, in step 2, to green -violet. (these color changes were caused by formation of complexes of chromium and carboxylic acid residues; see this *Jour.* **49**, 118). These compounds could not be separated out by shaking with ether. *Group 2*: butyric, valeric acids. With up to 3 mols of butyric acid and 2 mols of valeric acid, water soluble complexes were formed that behaved on aging like those of group 1. With greater proportions of acid, dark violet, amorphous, flocculent precipitates were formed. The water soluble compounds could be partially shaken out with ether and precipitated from the ether solution with alcohol. As a rule the precipitates (with more than 3 mols of butyric or 2 mols of valeric acid) were not soluble in organic solvents. *Group 3*: caproic, caprylic, capric acids. On mixing solutions of chromium chloride and the sodium salts of these fatty acids there was immediate turbidity and separation of violet oily drops that clung to the walls of the vessel and also formed a layer on the bottom of the solution. The slution changed from green to blue, but did not later turn green as was the case for group 2 solutions. With more than 8 mols of caprylate or 4 of caprate, bright violet emulsions formed that were stable for months. *Group 4*: lauric, myristic. palmitic, stearic acids. On mixing the solutions, voluminous, flocculent, not sticky precipitates formed at once. Bechause of the volume of the precipitate a maximum of 1.5 mols of acid per chromium atom was used. Except for lauric, which was colored at the start, the precipitates were white and changed to violet on aging. The fresh precipitates were soluble in ether and alcohol. After aging the precipitates were soluble in ether but precipitated from this solution on addition of alcohol. Chromium stearate under the trade name Quilon is marked as a water-proofing agent for leather (see R. K. Iler, Ind. Eng. Chem. 46, 766 (1954). The condtions necessary for formation of water soluble chromium stearate were found from experiments with chromium chloride in methyl alcohol brought to different basicities with alcohol sodium hydroxide. Chromium sulfate could not be used, because it could not be made basic enough. Also sodium stearate could not be used, because it would not give the required basicity. The following table shows the molar relations of stearic acid and chrome and the basicities required for water stable soaps:

	mols of stearic acid per chromium atom		
Basicity	0.5	0.33	0.25
20%	0	0	0
40%	0	30 min.	6-8 hours
60%	0	1 hour	1 week

The figures in the table above give the length of time during which the solutions remained clear after mixing the sodium stearate complex with water.
To form water stable compounds, the basic, alcoholic, chromium chloride solution and the stearic acid must be heated under a reflux condenser for some time. I.D.C.

The Numerical Evaluation and Properties of Vegetable Tanning Liquors. By D. Burton. *Das Leder*, **5**, 261 (1954). An address at the annual VGCT meeting in Hamburg, reviewing methods for determining acidity, salt content, and astringency of tan liquors. (see Burton and Bickley this Jour. 50, 55). Data are summarized in the following table: The ratio of salts of weak acids to total acidity (column F) does not measure astringency but, in general, this ratio is less than 1 for pyrogallol type tannins and greater than 1 for catechol type tannins..

A	B	C	D	E	F	G
Tanning material	Initial pH 20° Bk.	Total acidity	Total salts of weak acids	Astringency, $\frac{1000}{D}$	$\frac{D}{C}$	Class
Sonali bark, lX	5.68	9	470	2.1	52.3	c
Babul bark, lX	5.30	19	233	4.3	12.3	c
Avaram bark, lX	5.26	23	240	4.2	10.4	c
Gambier, sX	4.38	52	217	4.6	4.17	c
Mimosa. sX	4.56	22	66	15.0	3.00	c
Quebracho, sX	4.74	17	51	19.8	3.00	c
Goran bark, lX	4.34	48	75	13.3	1.60	c
Mangrove bark, lX	4.12	34	50	20.0	1.47	c
Oak bark, lX	3.88	132	160	6.2	1.21	m
Valonia. lX	3.80	165	142	7.0	0.86	p
Sumac, lX	4.30	235	370	2.7	1.57	p
Divi-divi, lX	3.40	217	100	10.0	0.46	p
Myrobalans, lX	3.43	291	107	9.3	0.37	p
Chestnut wood, sX	2.88	184	22	45.4	0.12	m

lX=liquid extract; sX=solid extract; c=catechol type tannin; p=pyrogallol type; m=mixture of c and p.

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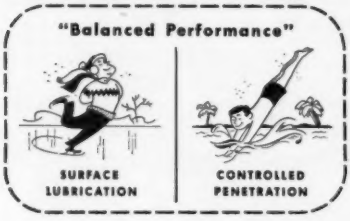

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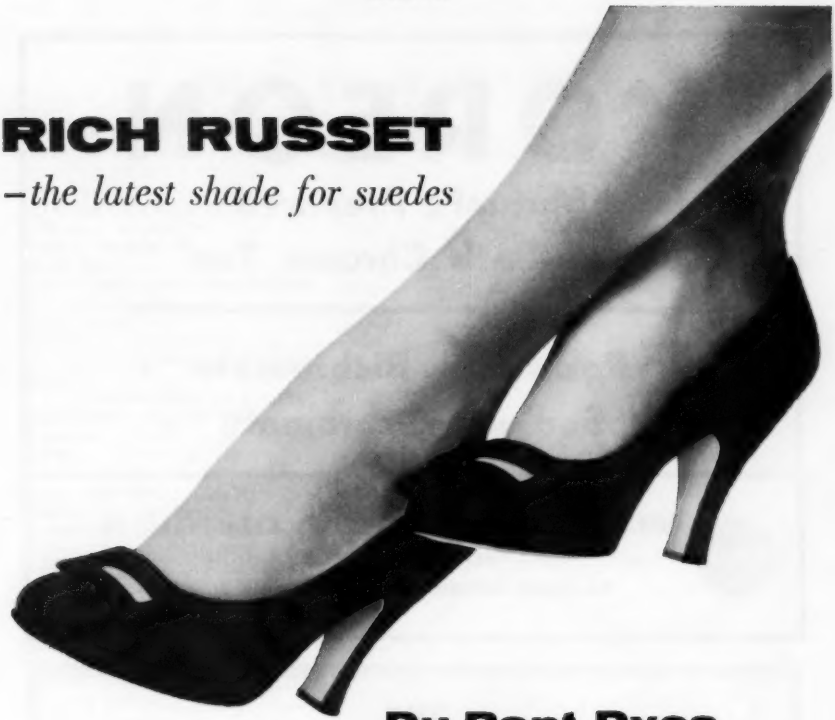
RICH RUSSET

—the latest shade for suedes



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give suede leathers full, bloomy undertones

The suede leather in these supple new shoes has been dyed a shade of russet with full, bloomy undertones and a soft, plushy look.

It was dyed with a level-dyeing, uniform combination of Du Pont dyes—dyes which produce full penetration and good fixation. *Result:* these high-style suede pumps, with the rich look and top color performance that will give them outstanding sales appeal all season long.

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Du Pont dyes recommended for russet shades:

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in

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The purpose of the laboratory is to conduct scientific research in the fields of Science concerned with Tanning and Leather.

To train Chemists in the technique of research and prepare them for Industry.

This Laboratory serves as the Official Technical Headquarters for the Tanning Industry of the United States.

Your inquiries will be gladly answered.

Address DR. FRED O'FLAHERTY, Director
Tanners' Council Laboratory
University of Cincinnati
Cincinnati 21, Ohio.

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Solid — Powder — Spray Dried

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MELLOWED CHESTNUT

Highly Soluble — Weight Giving — Good Color

MADE FROM LIVE WOOD

TYPICAL A.L.C.A. ANALYSIS

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NON-TANNIN	21.65	26.67	19.1
INSOLUBLES	.65	.67	.7
WATER	15.98	6.71	6.7

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TYPICAL A.L.C.A. ANALYSIS

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INSOLUBLES	1.70	0.72
WATER	20.72	17.80

Also Available as Liquid with 30% Tannin

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